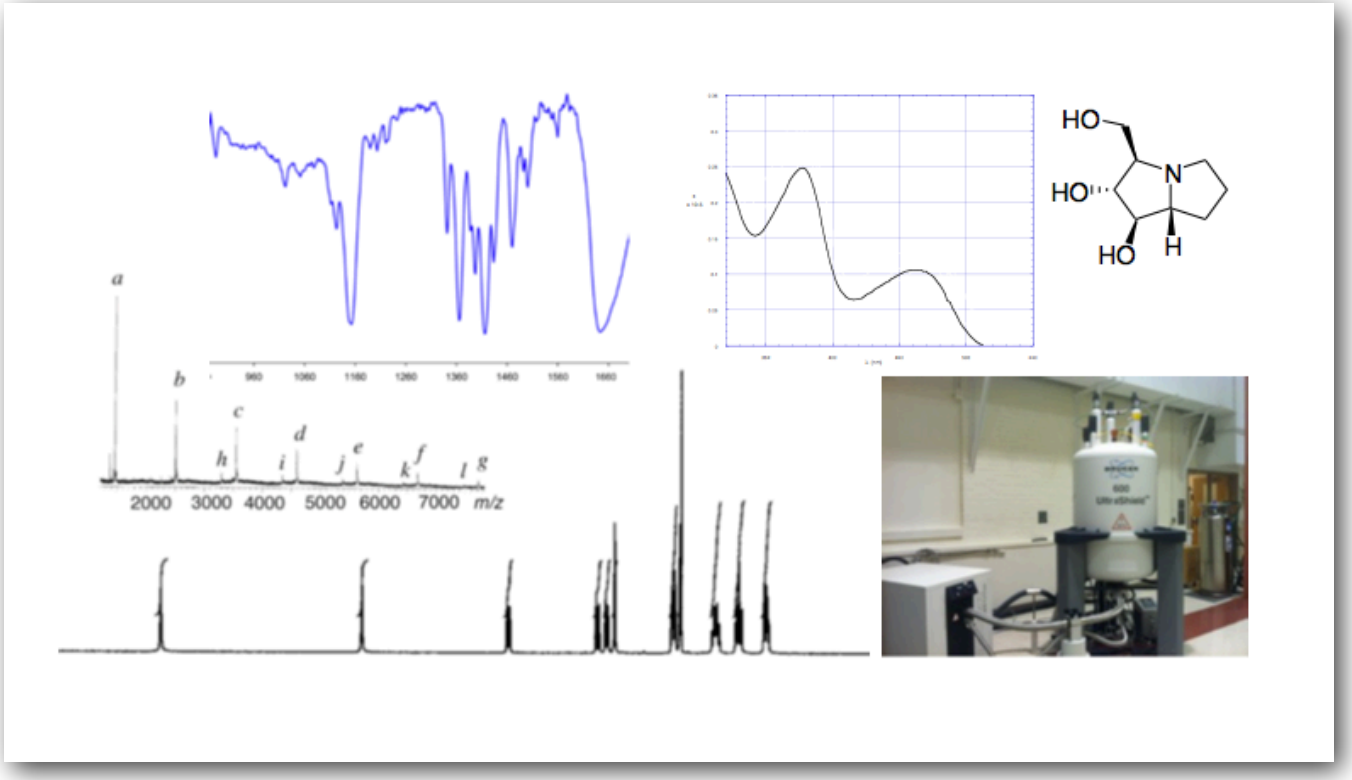
Chem 333

Organic Spectroscopic Structure Determination & Organic Lab for Majors



Professor Joseph M. Fox,
212 Lammot Du Pont Laboratory, 302-831-0191 , jmfox@udel.edu
Lectures are held in Wolf 100, Mondays 3:35–5:35 pm
Office hours: Mondays 11-12, or by appointment. Contact me by email to schedule appointment

syllabus

Course:
http://www.udel.edu/chem/fox/Chem333/Fall2013/Chem333Fall2013/Welcome.html

Laboratory:
https://sakai.udel.edu/portal/site/4d966bd4-c04b-4b73-97fd-df1989cdb2fc

Lab

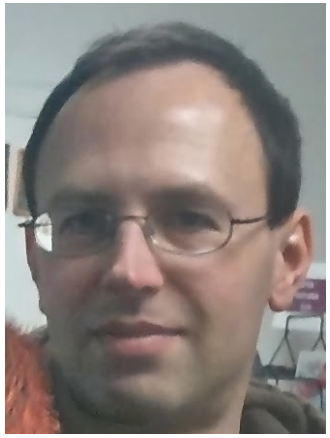
The director of the organic teaching laboratories is Dr. Geoffrey Sametz sametz@UDel.Edu

QUESTIONS ABOUT THE LABORATORY SHOULD BE DIRECTED TO DR. SAMETZ

The laboratory syllabus can be found here: https://sakai.udel.edu/portal/site/4d966bd4-c04b-4b73-97fd-df1989cdb2fc

Safety

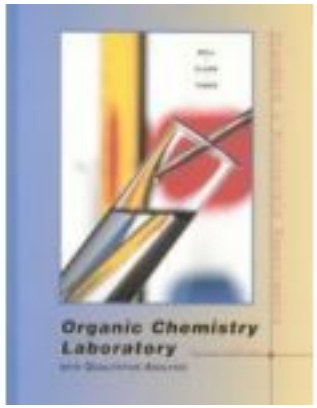
You Must Have Safety Goggles
No Shorts
No Open Toed Shoes
No Food or Drink
Come Prepared, Read the Assignment, and Bring your Notebook



Books

Bring em
To class

"lab manual"



If you are

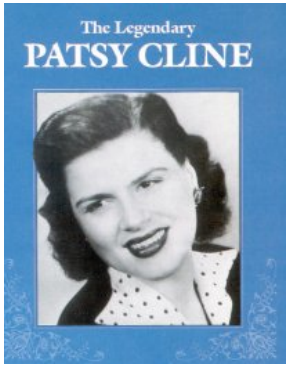
taking lab

Section 010

or

"Spec book"

If you are in
section 011 and
NOT taking lab



Chapters 11-14 are available as handout and have been uploaded to website

clickers

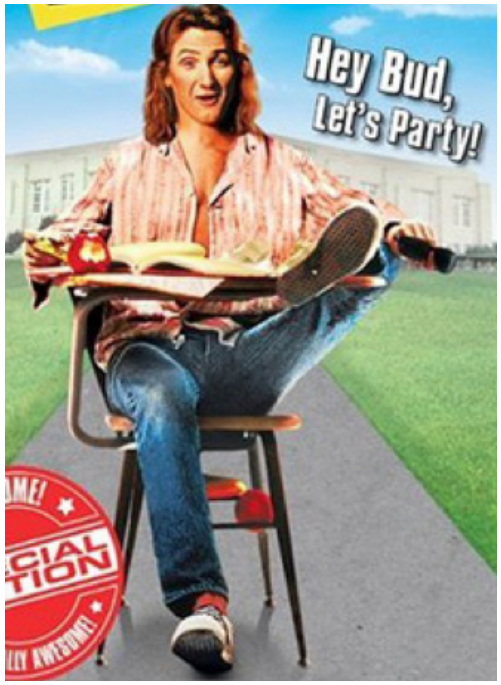
Either generation of clickers (gen 1 or 2) will work for this class.

grading

Grading for the lecture part of this course will be determined based on the average (50% each) of a midterm and final exam.
Midterm will be in class on 10/21
Final will be during finals week

Chem 333 lecture : only 1 credit for all of this work?

- take it easy?



- essential information for Chem 331, and 333/334 next semester

Upcoming Lecture schedule

Lecture 1: Introduction to Structure Determination by Spectroscopy; IHD and 13C NMR spectroscopy.

READ: Chapter 12 in Bell, Clark and Taber or Chapter 1 in Organic Spectroscopic Structure Determination

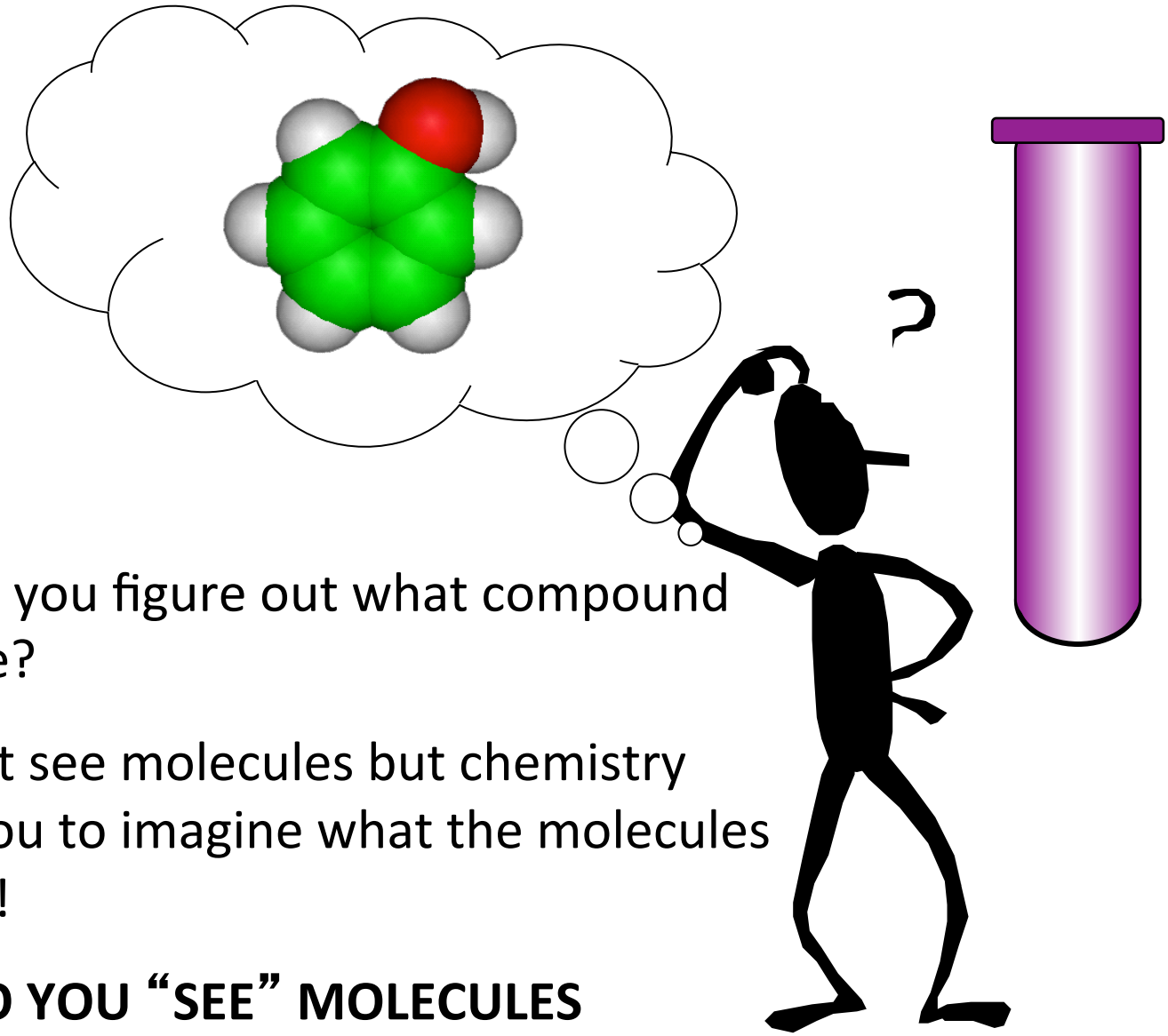
HANDOUT: 13C LECTURE NOTES, 13C NMR TABLES

PROBLEMS: Complete end of chapter 12 problems 1–10 from Bell, Clark and Taber
Answers

Lecture 2 (9/16): Problem Solving with 13C NMR spectroscopy (note: video link will be posted)

PROBLEMS: Complete end of chapter 12 problems 11–20 from Bell, Clark and Taber
Answers

WHAT IS THIS COURSE ABOUT??

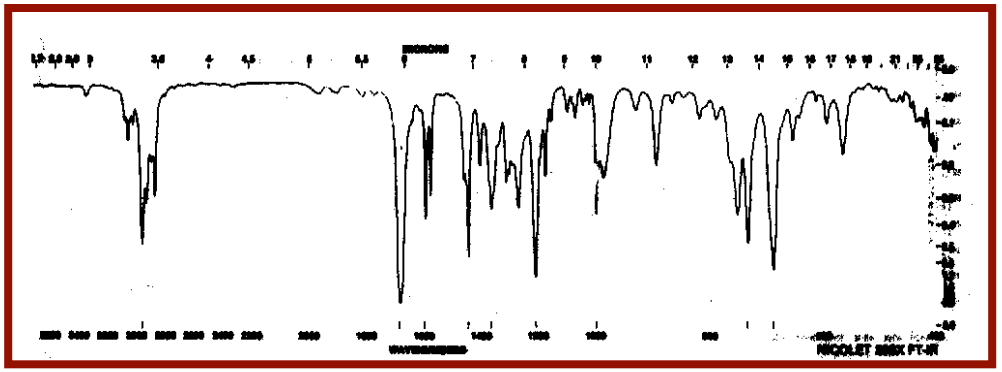


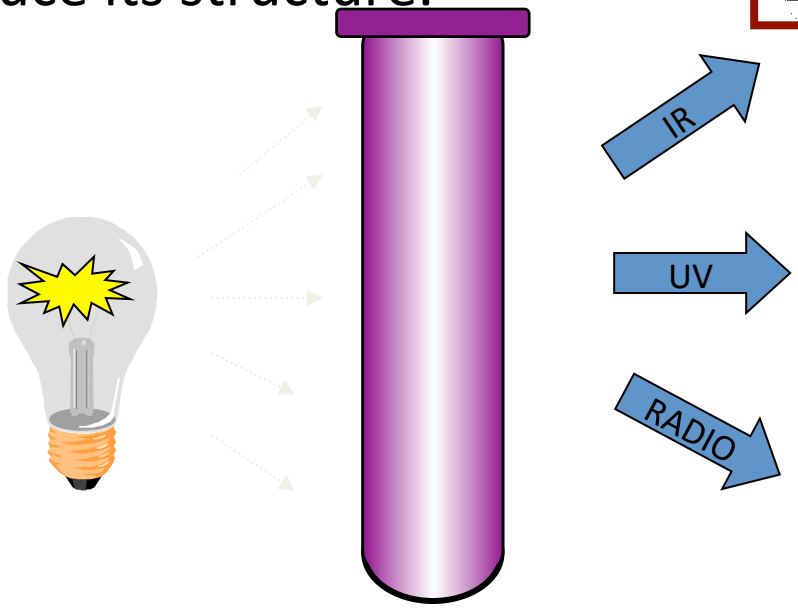
How can you figure out what compound you have?

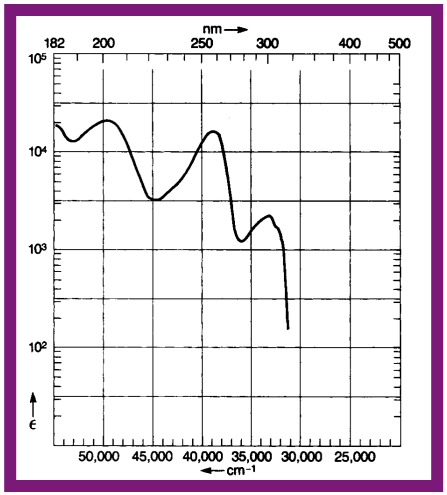
You can't see molecules but chemistry allows you to imagine what the molecules look like!

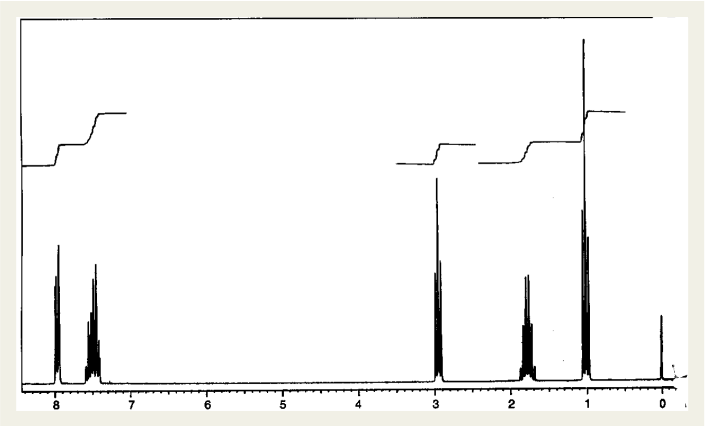
HOW DO YOU "SEE" MOLECULES

By shining light through samples, we can learn about the molecular structure of the sample and (sometimes) deduce its structure.









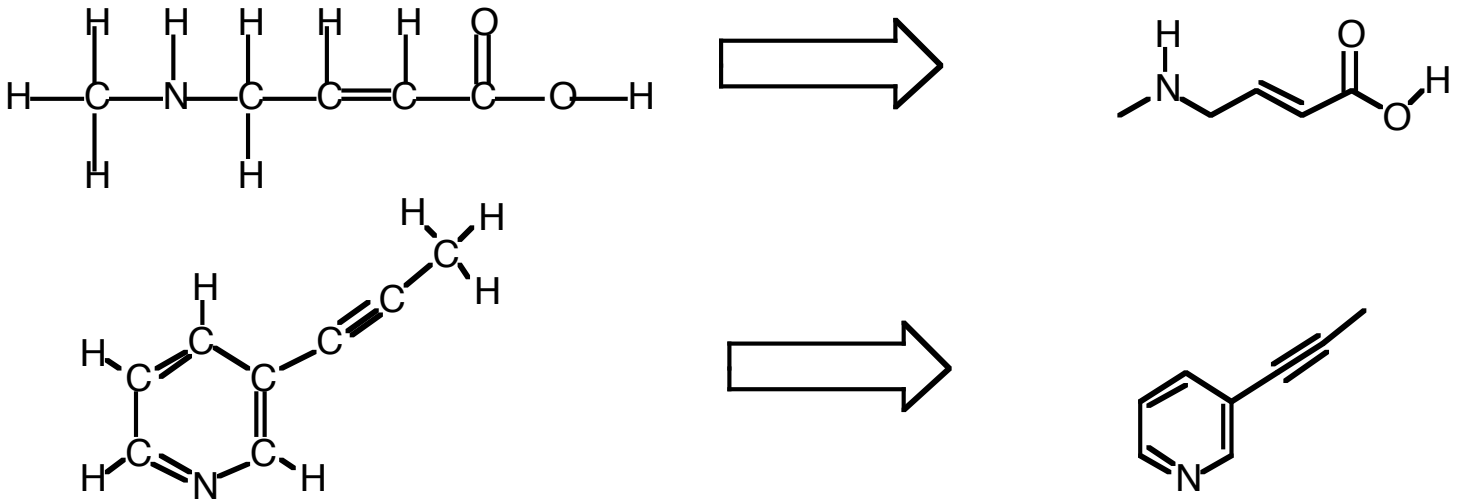
By the end of this course you will be able to interpret these light absorbing properties of molecules and deduce molecular structures!

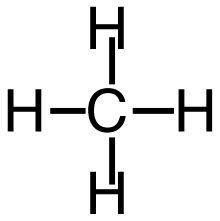
Basics:

Bond-Line Formulas

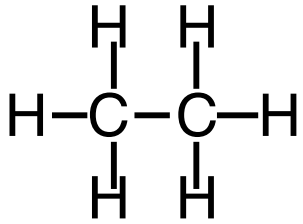
We will quickly be using bond-line formulas, an organic chemists shorthand for molecular structurres, to represent molecular structures. It is imperative that you learn to read and draw bond line formulas too.

(hint: O likes 2 bonds; N likes 3bonds)





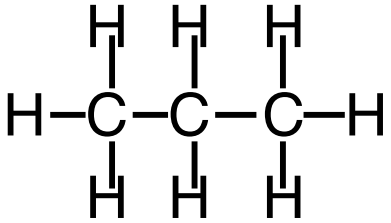
C_1H_4



C_2H_6

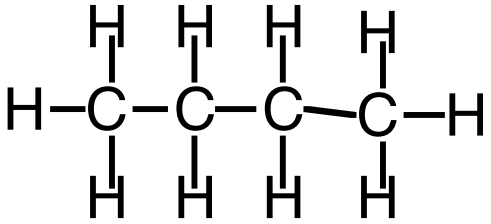
Saturated alkanes (CH only compounds) have the general formula:

$$C_NH_{2N+2}$$

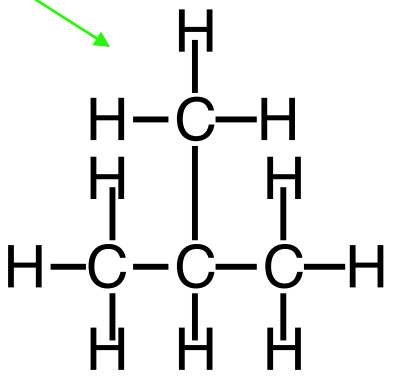


C_3H_8

Note: it doesn't matter how the atoms are configured:

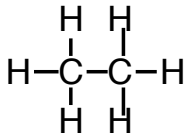


C_4H_{10}

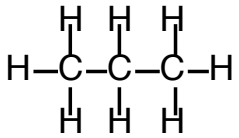


C_4H_{10}

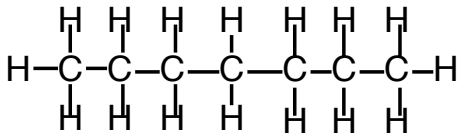
C_NH_{2N+2}



C_2H_6

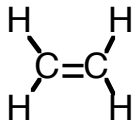


C_3H_8

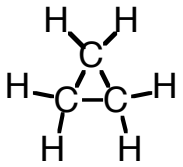


C_7H_{16}

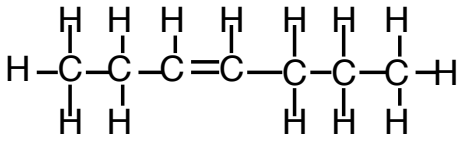
C_NH_{2N}



C_2H_4

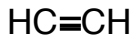


C_3H_6

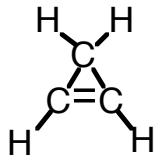


C_7H_{14}

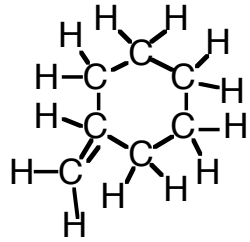
C_NH_{2N-2}



C_2H_2



C_3H_6



C_7H_{12}

Two less hydrogens per double bond or ring!

The molecular formula can tell you about the structure:

FORMULA TELLS US THE NUMBER OF DOUBLE BONDS OR RINGS:

IHD = index of hydrogen deficiency.

a.k.a. Degree of unsaturation.

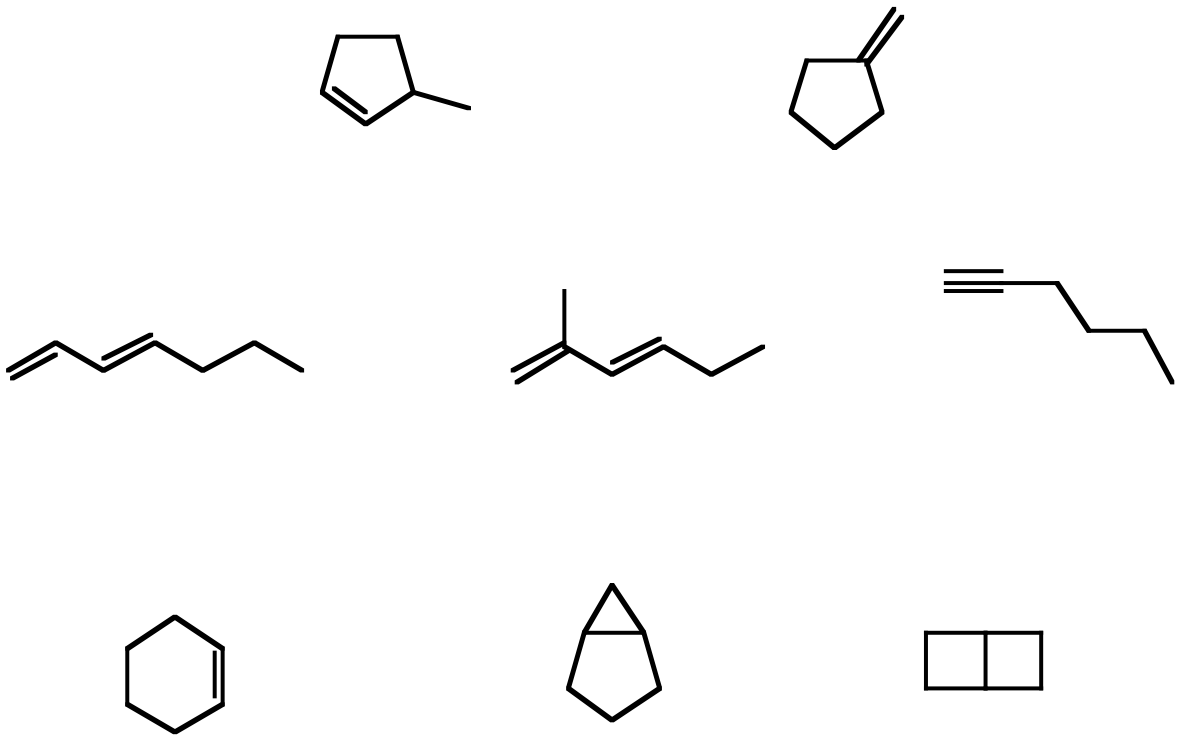
For $C_N H_Y$

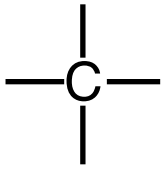
$$IHD = \frac{[2N+2]-Y}{2}$$

Example: C_6H_{10}

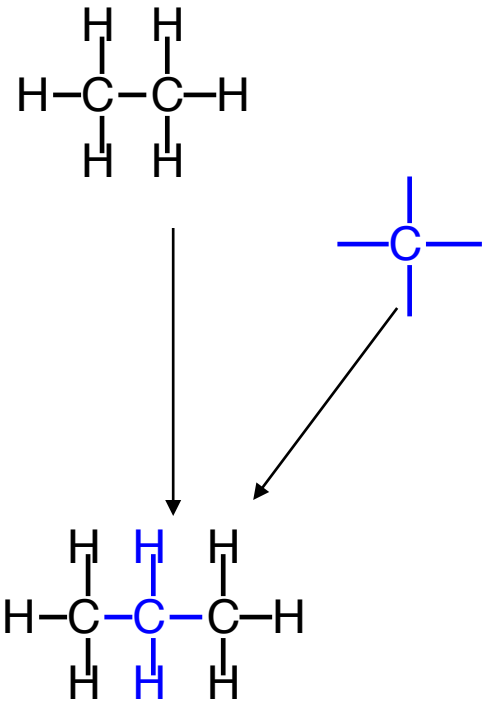
$$IHD = \frac{[(6 \times 2)+2]-10}{2} = \frac{4}{2} = 2$$

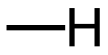
- Two double bonds
- Two rings
- One triple bonds
- One double bond plus one ring

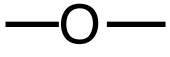


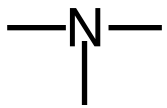


For each Carbon (valence =4) you add to a structure requires the addition of two more Hydrogens









X =

—F

—Cl

—Br

—I

Each halogen (valance = 1), takes the place of a hydrogen

Oxygen (valance = 2) can be added into a structure without changing the number of hydrogens

Each added nitrogen (valence =3) requires one additional hydrogen

For C_NH_YXON

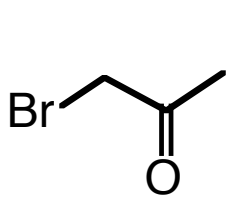
$$IHD = \frac{[2N+2]-Y-(\#halogens)+(\#Ns)}{2}$$

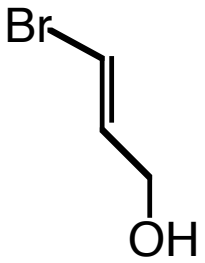
Example:

C_3H_5BrO

$$IHD = \frac{[(3 \times 2)+2]-5-1}{2}$$

IHD = 1



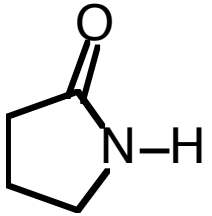


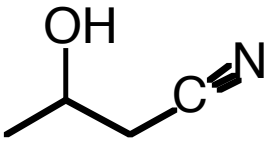
Example:

C_4H_7NO

$$IHD = \frac{[(4 \times 2)+2]-7+1}{2}$$

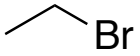
IHD = 2





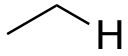
IHD shorthand

halogens (I, Br, Cl, F): give an H



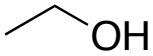
C_2H_5Br

same IHD as



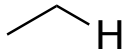
C_2H_6

oxygen family (O, S, Se): no effect on IHD



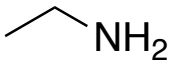
C_2H_6O

same IHD as



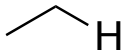
C_2H_6

nitrogen family (N, P): take an H



C_2H_7N

same IHD as



C_2H_6

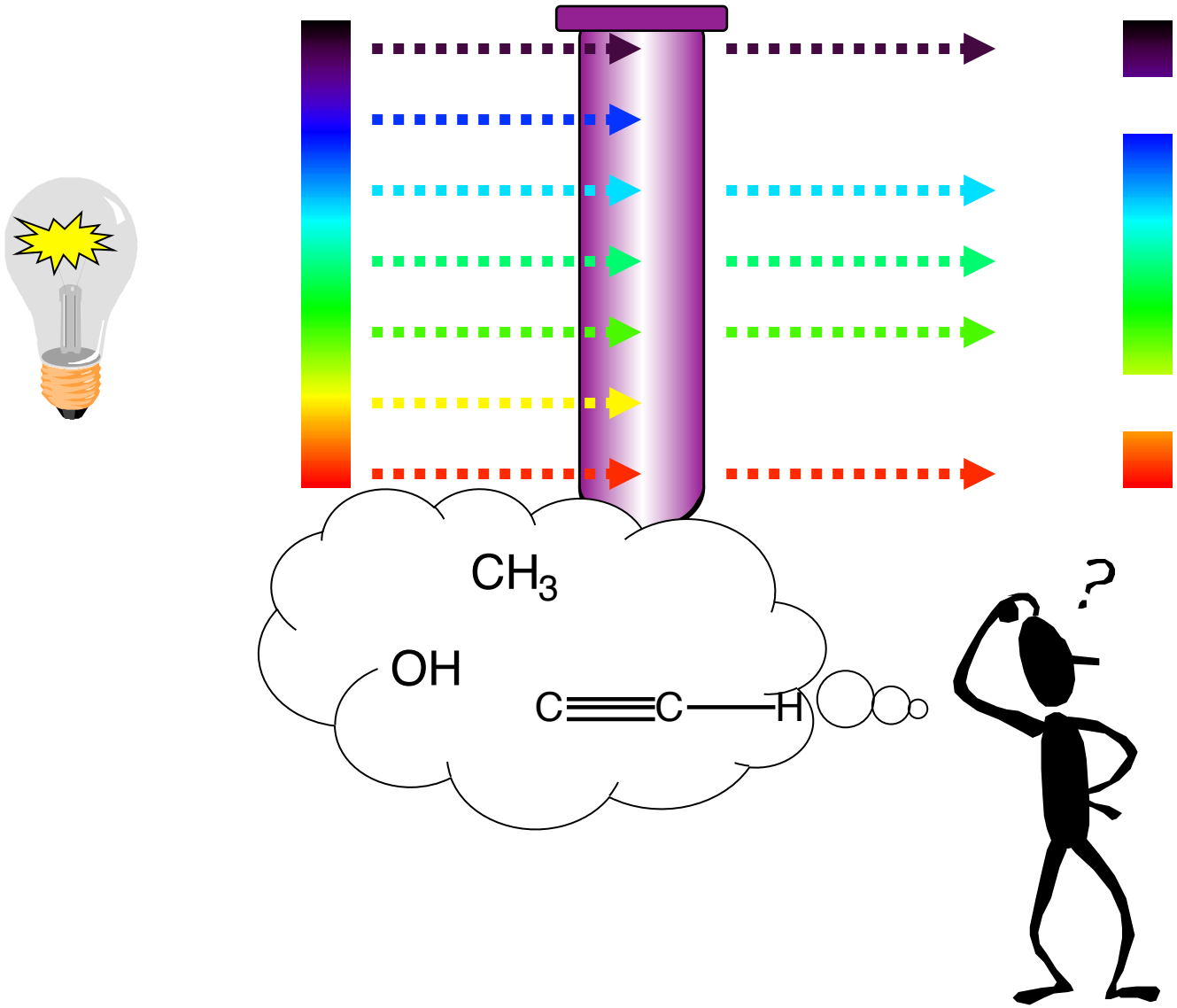
Note: this slide
Not in your handout
But I will post it tonight

Clicker questions

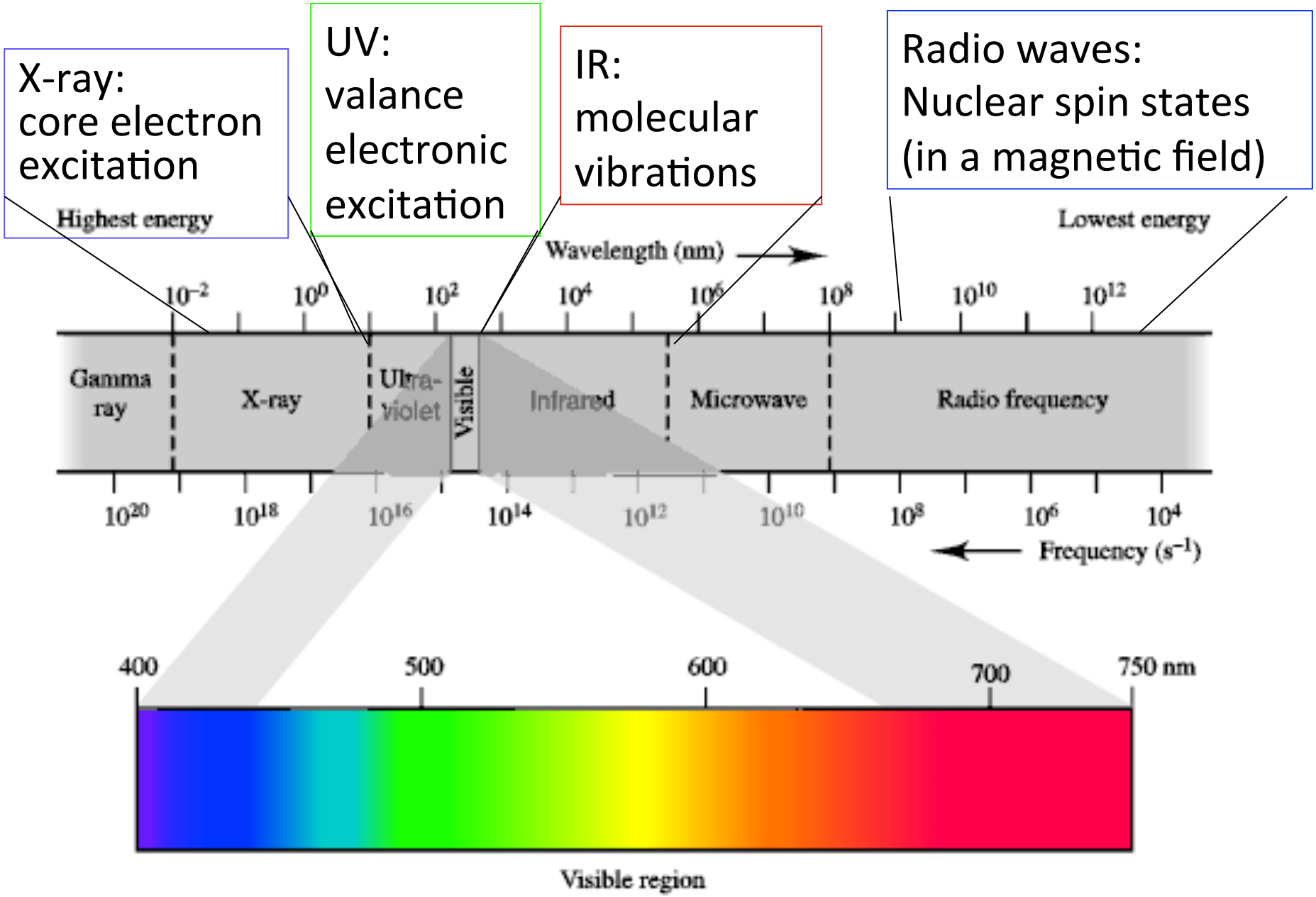
	has same IHD as as			
C_4H_8O	a. C_4H_8 IHD = 1	b. C_4H_{10} IHD = 0	c. C_4H_6 IHD = 2	d. C_4H_4 IHD = 3
C_5H_9BrO	a. C_5H_8 IHD = 2	b. C_5H_{10} IHD = 1	c. C_5H_{12} IHD = 0	d. C_5H_6 IHD = 3
C_6H_7N	a. C_6H_{14} IHD = 0	b. C_6H_{12} IHD = 1	c. C_6H_{10} IHD = 2	d. C_6H_6 IHD = 4
C_5H_5N	a. C_5H_{12} IHD = 0	b. C_5H_{10} IHD = 1	c. C_5H_8 IHD = 2	d. C_5H_4 IHD = 4
C_6H_6FNO	a. C_6H_6 IHD = 4	b. C_6H_8 IHD = 2	c. C_6H_{12} IHD = 1	d. C_6H_{14} IHD = 0

Note: this slide not in your handout but I will post it tonight

We can tell something about the molecules you have by the frequencies of light it absorbs

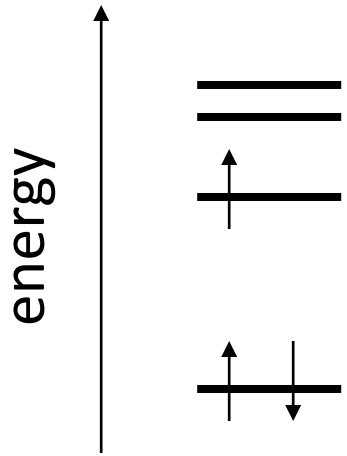


Different frequencies of light (electromagnetic radiation) interact with different aspects molecular motion (potential and kinetic energy).

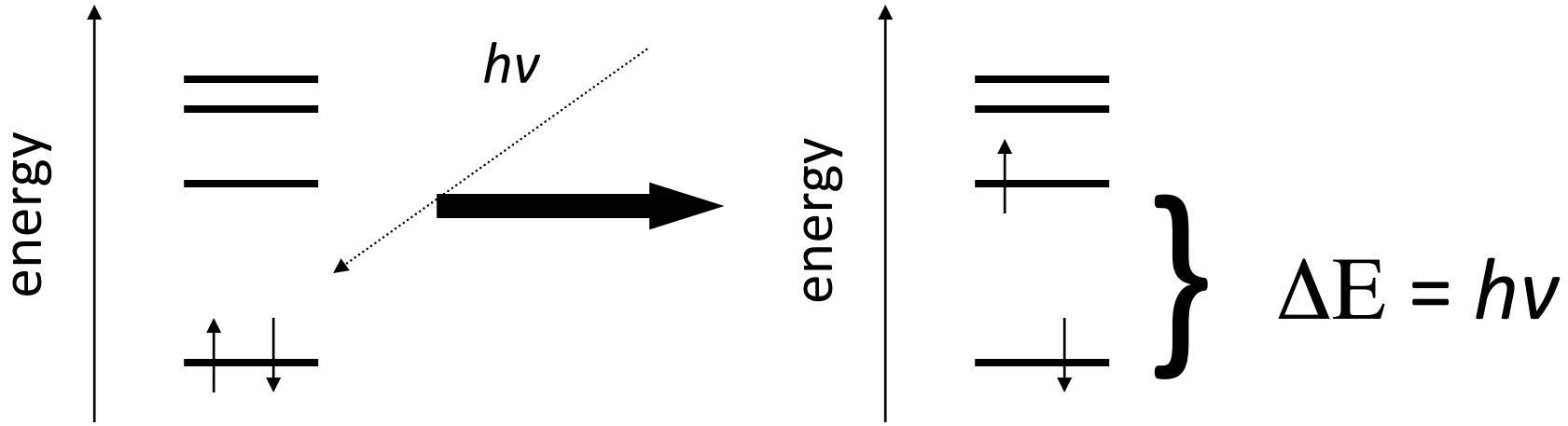


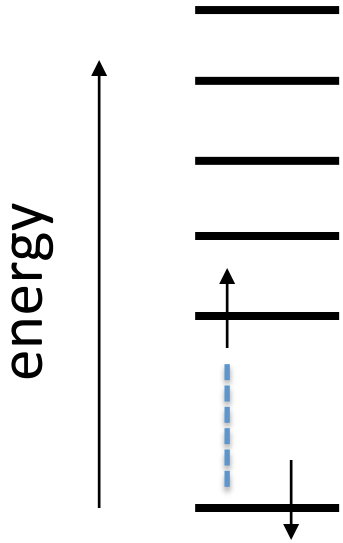
Molecules have quantized energy levels

ex. electronic energy levels.



General Principle of Spectroscopy: A molecule absorbs light when the frequency of light correlates with an energy transition.

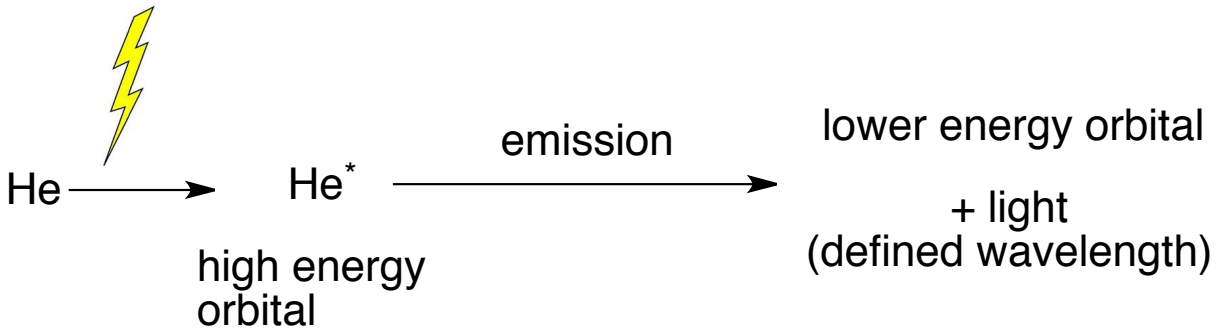




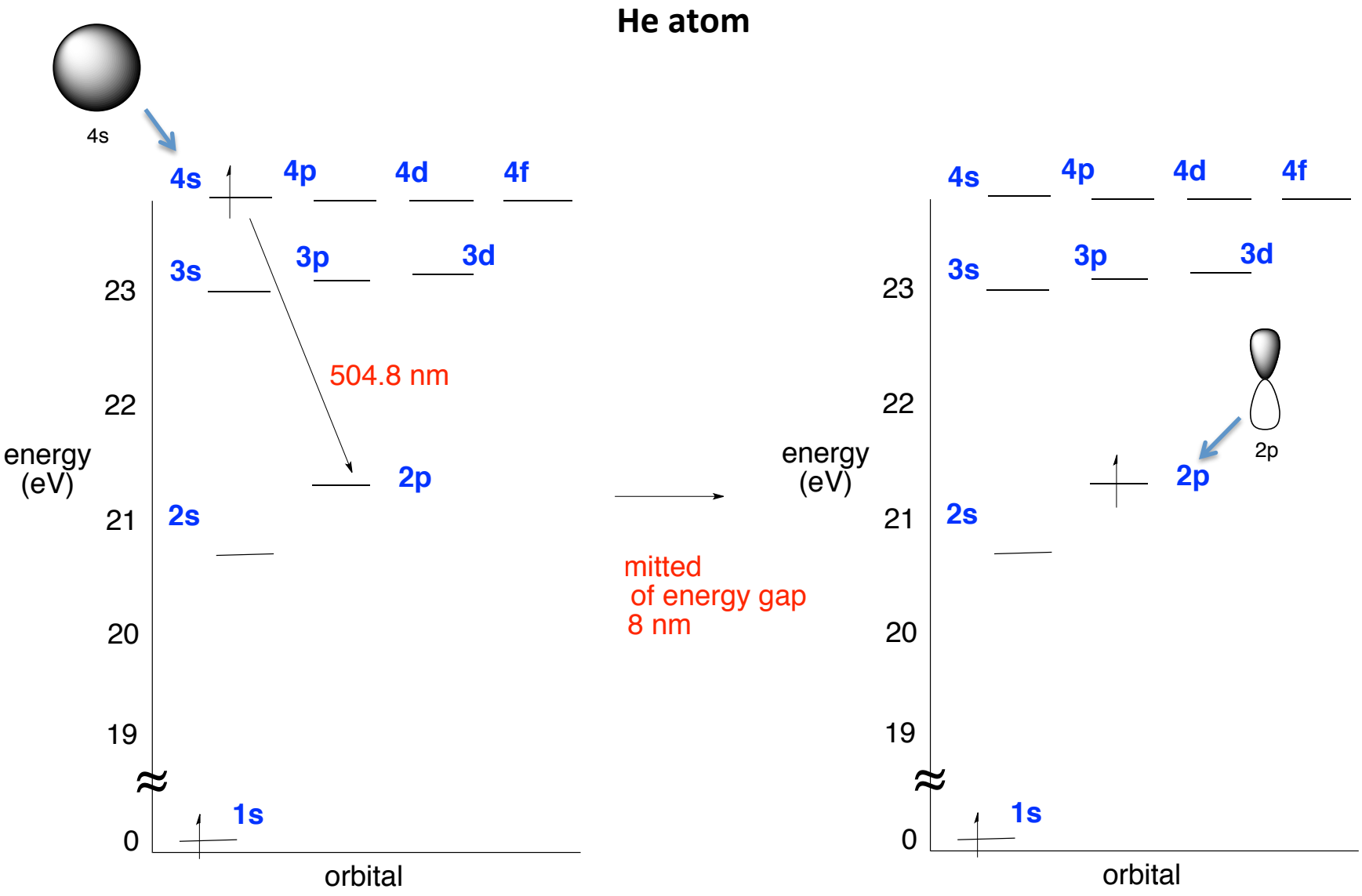
northeastmaglev.com -

Electronic energy levels are quantized

When an electric current is passed through a glass tube that contains helium gas at low pressure the tube gives light

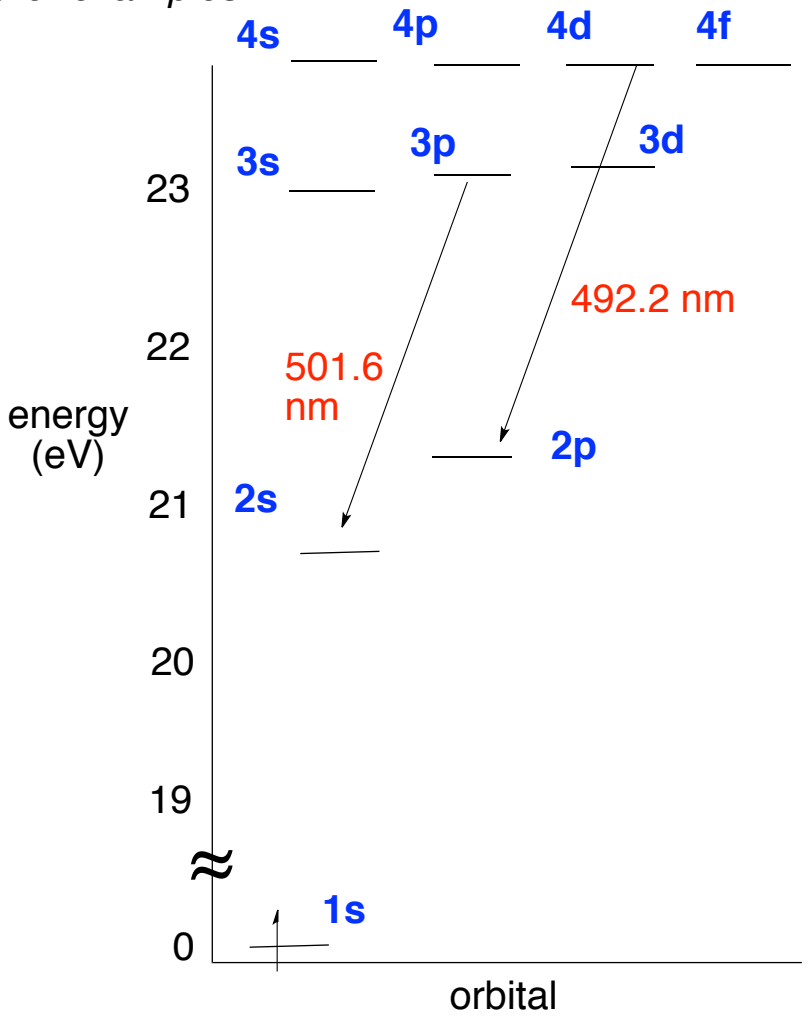


Recall: Electronic energy levels are quantized

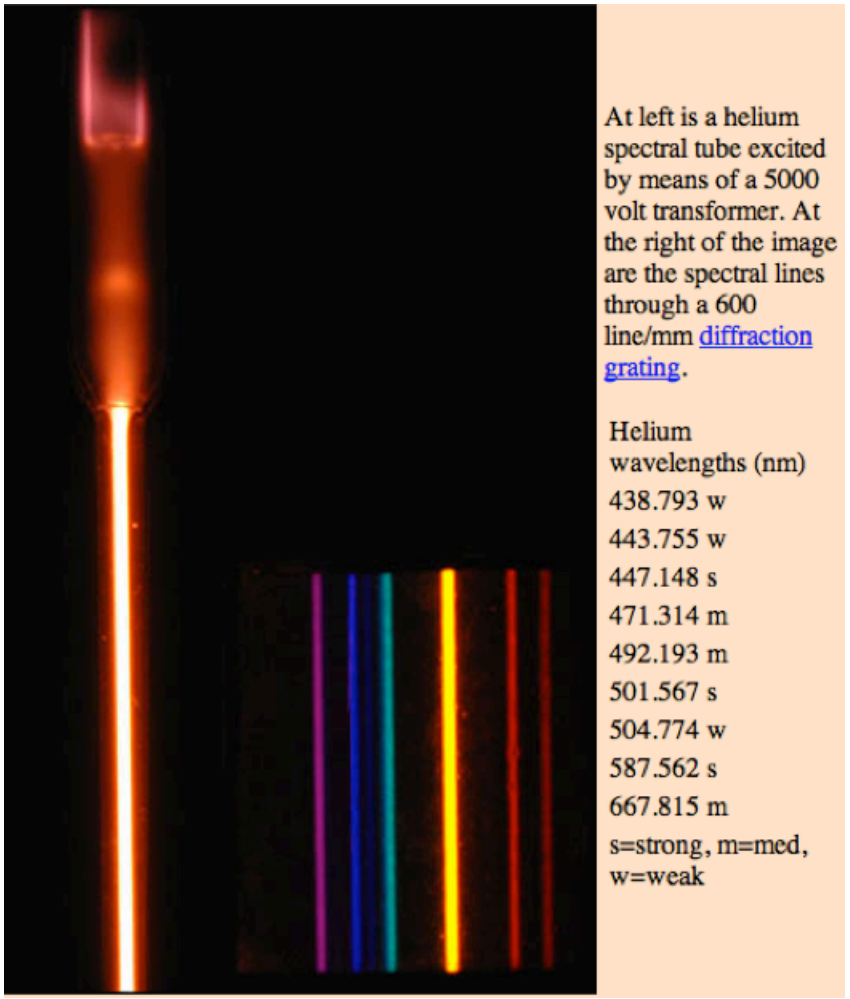


Recall: Electronic energy levels are quantized

other examples



So when light is emitted from helium ions, we see discrete bands, not a continuum of emitted light



At left is a helium spectral tube excited by means of a 5000 volt transformer. At the right of the image are the spectral lines through a 600 line/mm diffraction grating.

Helium wavelengths (nm)
438.793 w
443.755 w
447.148 s
471.314 m
492.193 m
501.567 s
504.774 w
587.562 s
667.815 m
s=strong, m=med, w=weak

http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/atspect.html#c1

Nuclear energy levels are also quantized

Associated with each nuclear spin is a nuclear magnetic moment which produces magnetic interactions with its environment.

The nuclear spins for individual protons and neutrons parallels the treatment of electron spin, with spin 1/2 and an associated magnetic moment. The magnetic moment is much smaller than that of the electron.

Nuclear Magnetic Resonance

- The study of very low energy transitions of atomic nuclei with nuclear spin
- Some (not all) nuclei have spin. Only atoms with an odd number of protons or neutrons (or both) have nuclear spins that can be observed by NMR. : e.g. ^{13}C, ^{1}H.
- The most important technique in organic chemistry

nuclear transitions are little

1.4 mm
0.00086 eV
2 cal/mol

radiowaves

www.oldschoolhiphoprap.com

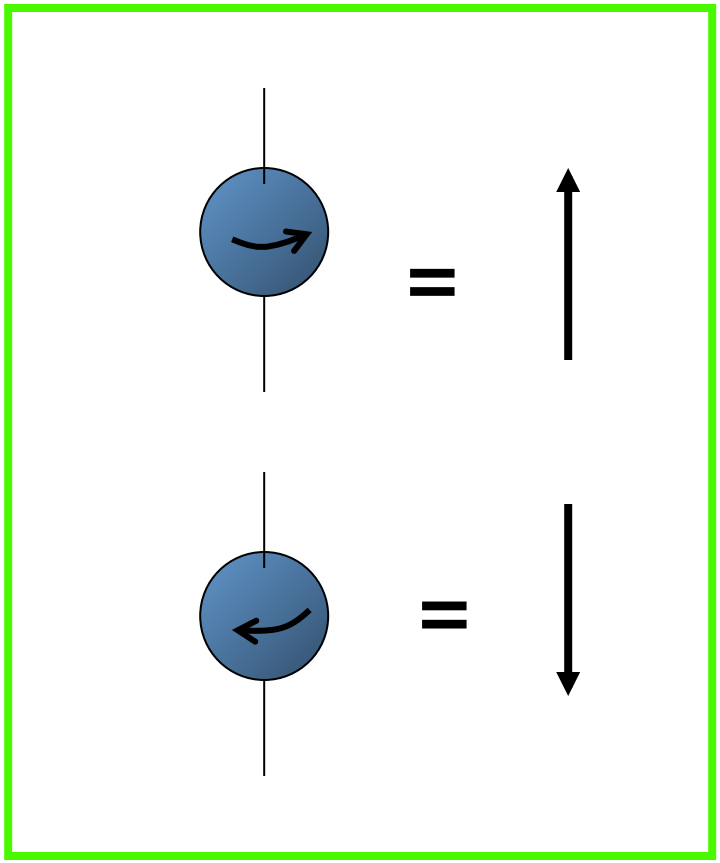
electronic transitions are big

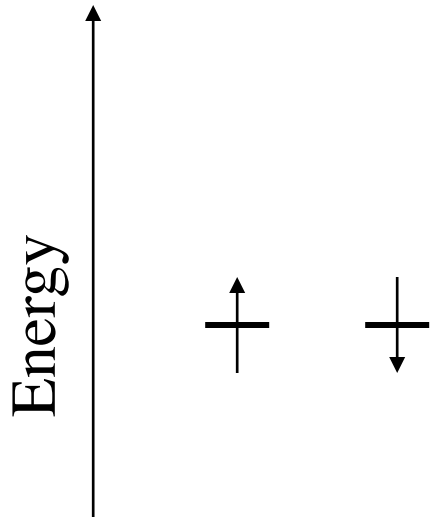
500 nm
2.5 eV
50,000 cal/mol

UV-vis

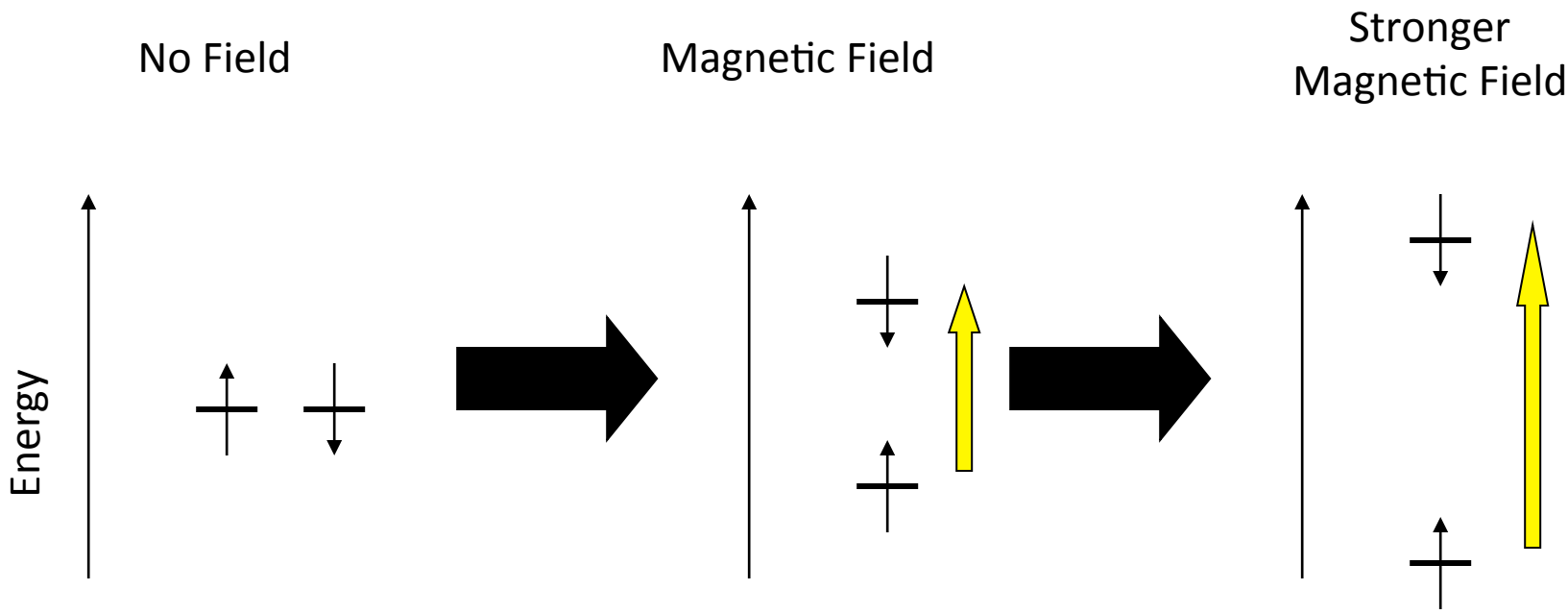
www.visionproeyecare.com

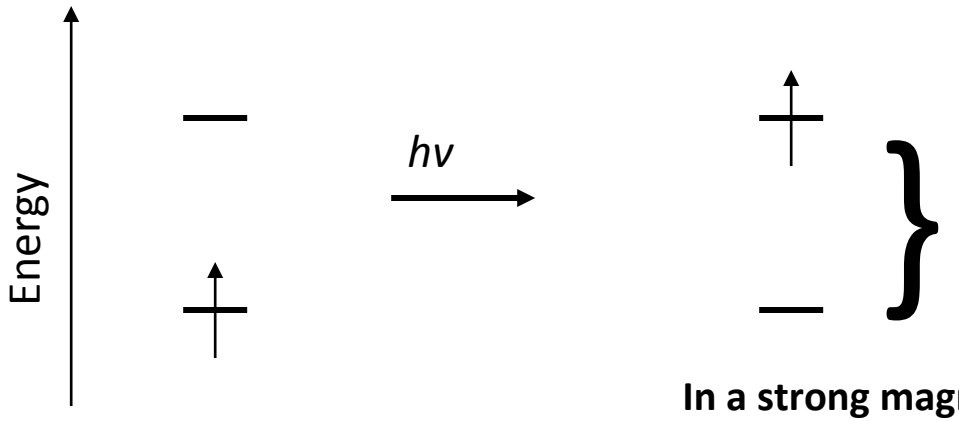
• NMR exploits the fact that many nuclei behave as magnetic dipoles in the presence of an external magnetic field





In the absence of a magnetic field, both spin states have equal energy

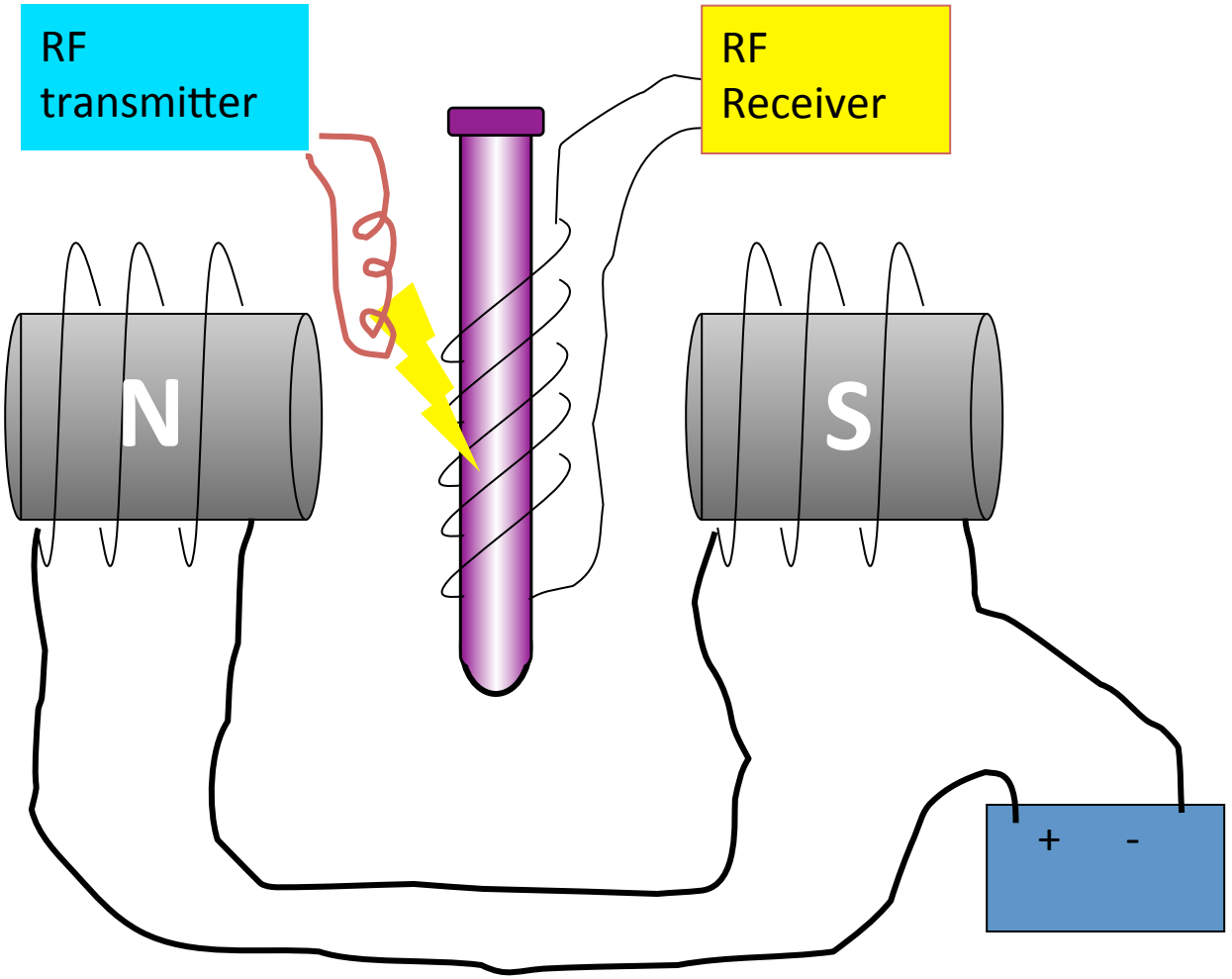




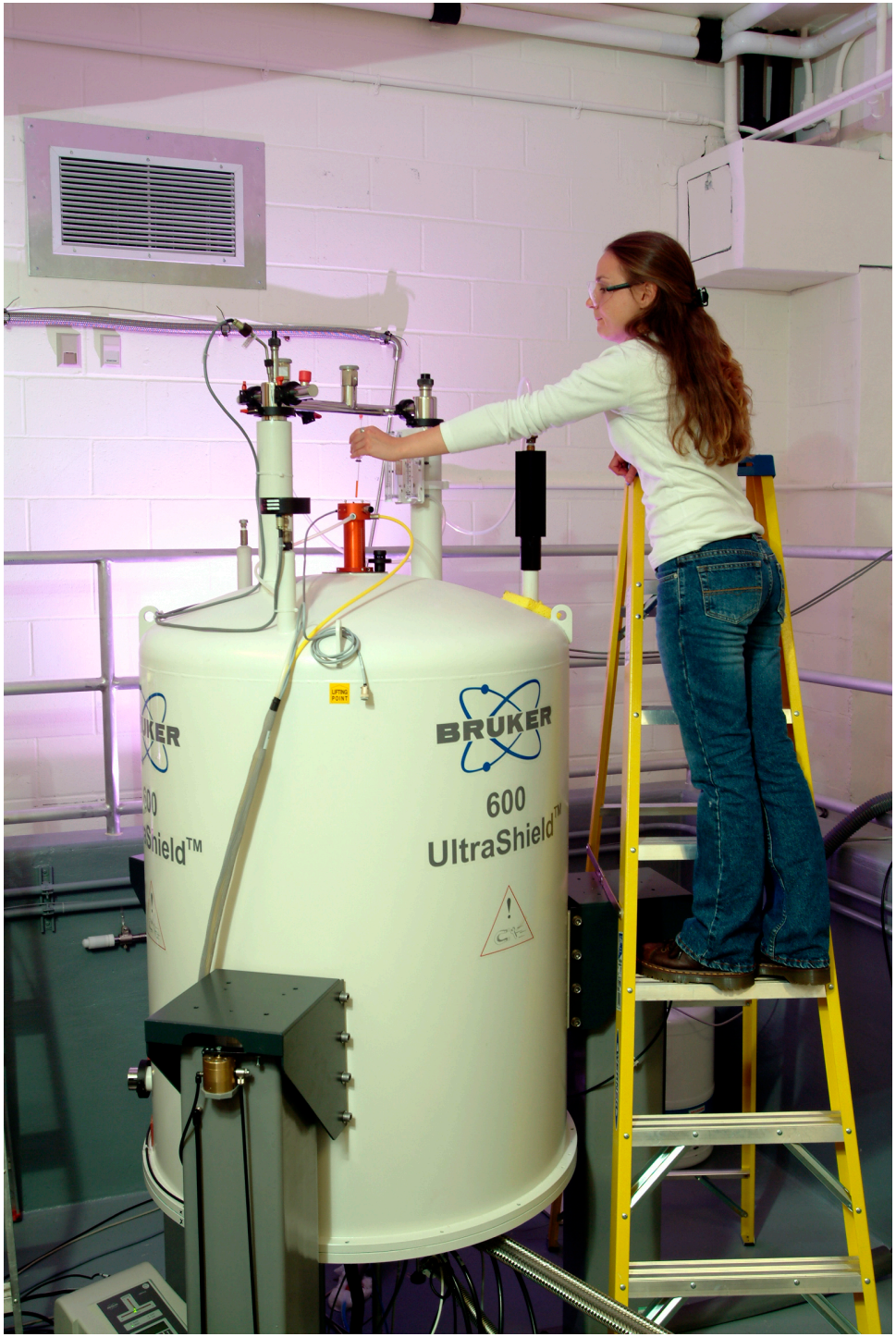
$$\Delta E = h\nu$$

In a strong magnetic field, the energy level difference corresponds to the energy of radio waves

How an NMR spectrometer works:



Note modern NMRs use superconducting magnets to attain very strong magnetic fields


BRUKER
600
UltraShield™


BRUKER
600
UltraShield

^{13}C-NMR

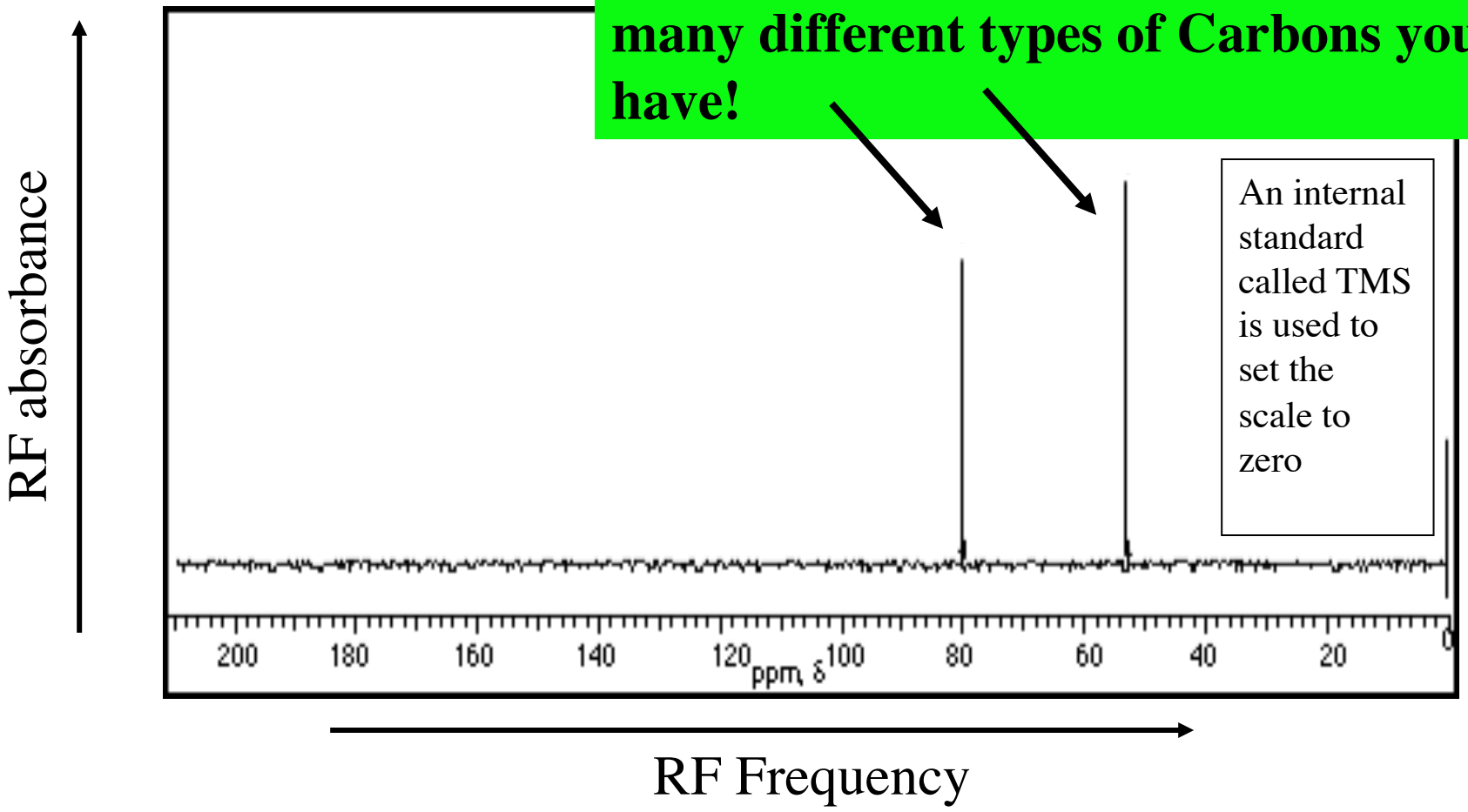
We can examine the nuclear magnetic properties of carbon atoms in a molecule to learn about a molecules structure.

NOTE: most carbons are ^{12}C. ^{12}C has an even number of protons and neutrons and cannot be observed by NMR techniques. However approximately 1% of carbons are ^{13}C, and these we can see in the NMR. (this will be come later when we consider nuclear spin coupling)

A ^{13}C-NMR spectrum.

<u>Here is what's cool about ^{13}C-NMR:</u>

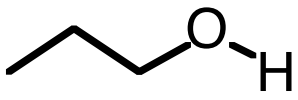
Different carbons appear at different frequencies! - Now you know how many different types of Carbons you have!

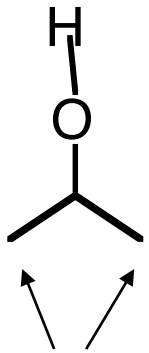


The intensity of the peak doesn't does not necessarily correlate to the number of carbons.

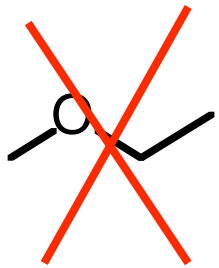
Example: Two alcohols (-OH compound) with formula C_3H_8O

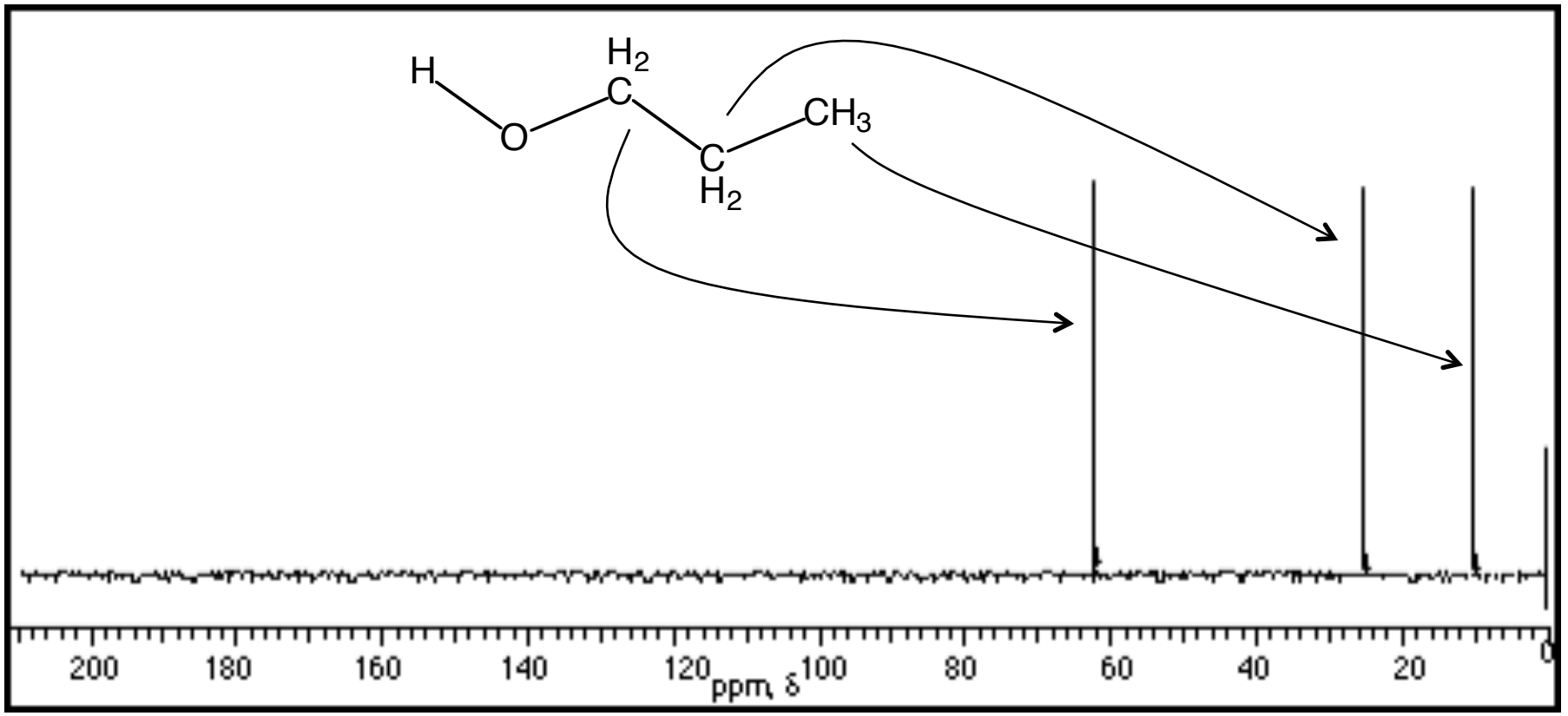
1. IHD = 0
2. Possible structures:



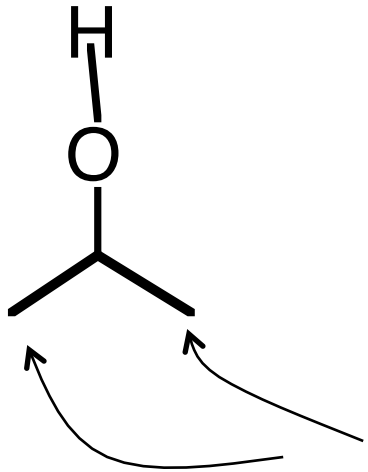


Same!

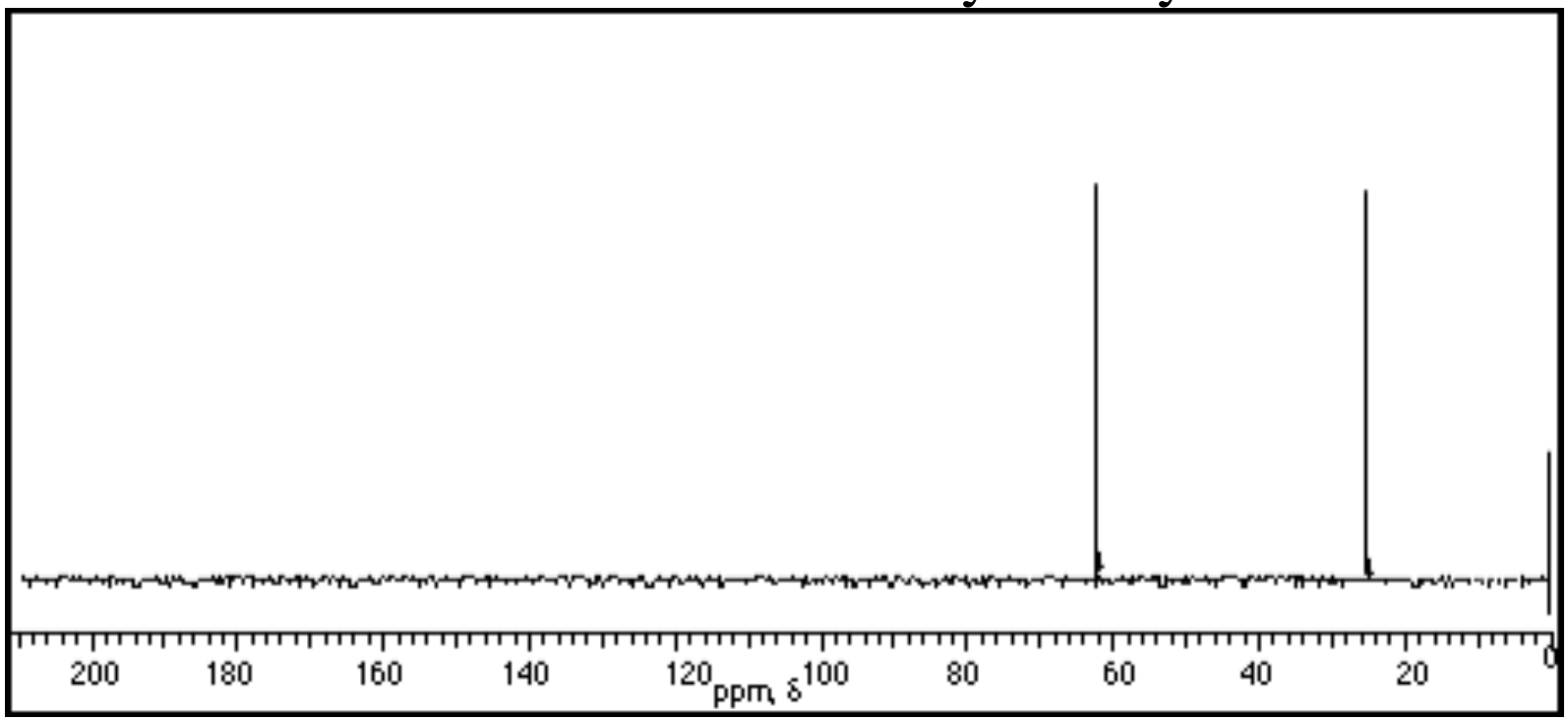




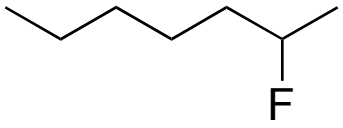
The C-NMR spectrum of isopropanol only shows two different carbons!



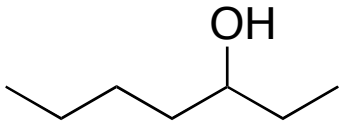
These two carbons are identical by symmetry:



How Many ^{13}C NMR resonances?



7



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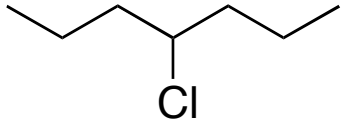
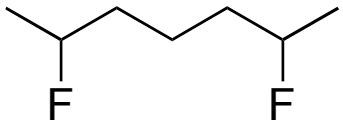
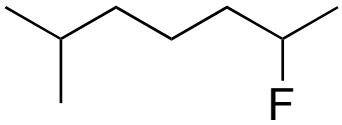


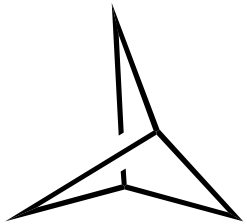
4



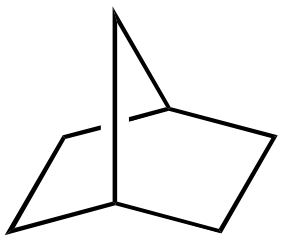
4



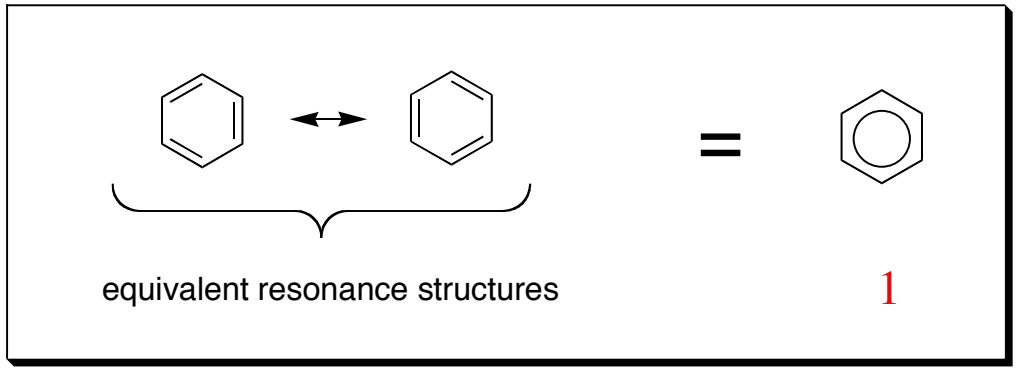
7

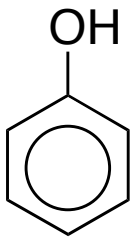


2

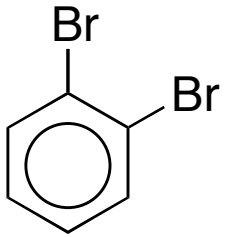


3

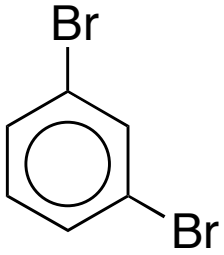

=
equivalent resonance structures
1


OH

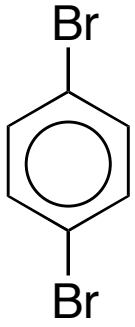
4


Br
Br

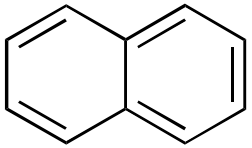
3


Br
Br

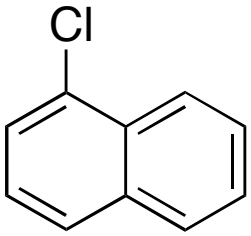
4


Br
Br

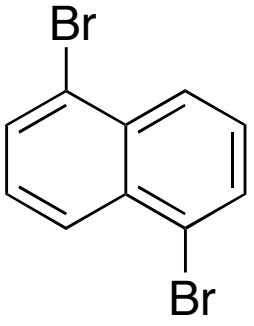
2



3


Cl

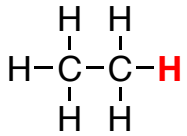
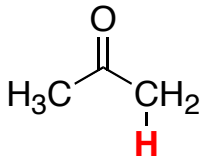
10


Br
Br

5

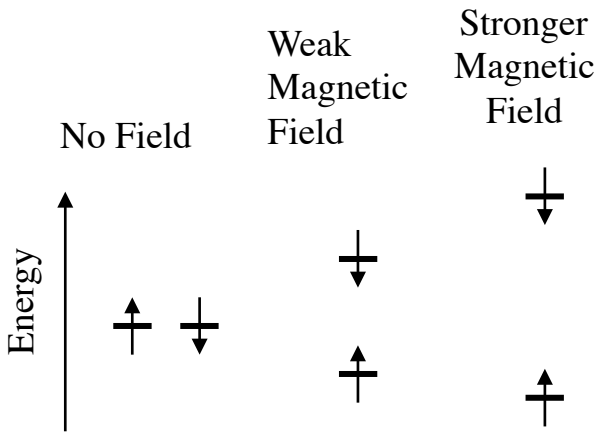
How do report the position of a different nucleus?

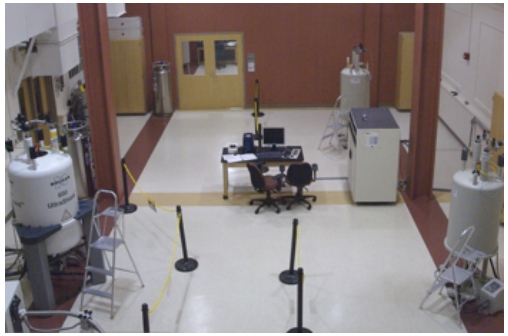
Just measure the frequency— easy?

60 MHz NMR		**300 MHz NMR**
60,000,060 Hz		300,000,300 Hz
60,000,130 Hz		300,000,650 Hz

Different spectrometers will give different numbers :(

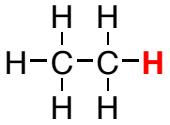
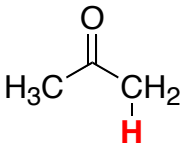
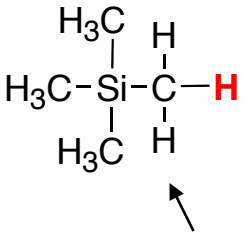
pipeline.corante.com





The solution: chemical shift (δ)

$$\delta = \frac{\Delta\nu \text{ relative to TMS (Hz)}}{\nu \text{ of spectrometer (MHz)}} \quad \textit{in ppm}$$

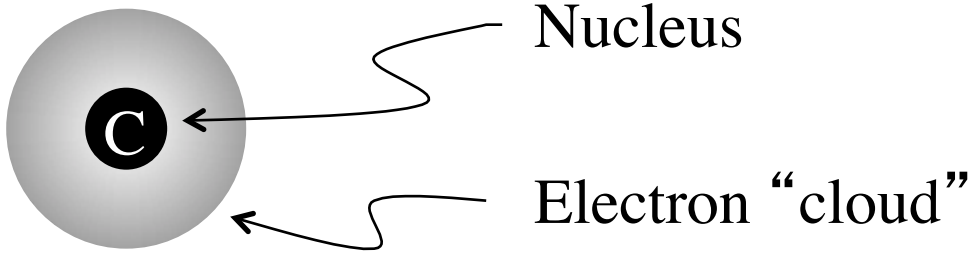
	60 MHz NMR		**δ**		**300 MHz NMR**
	60,000,060 Hz	60 Hz / 60 MHz	**1.00 ppm**	300 Hz / 300 MHz	300,000,300 Hz
	60,000,130 Hz	130 Hz / 60 MHz	**2.16 ppm**	650 Hz / 300 MHz	300,000,650 Hz
	60,000,000 Hz	(reference)	**0 ppm**	(reference)	300,000,000 Hz

TMS: tetramethylsilane, a reference standard

Different spectrometers will give the same numbers :)

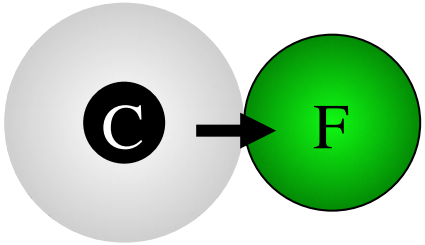
Why do nuclei in different environments appear at different frequencies?

An isolated ^{13}C atoms have the same chemical shift. (resonate at the same frequency)



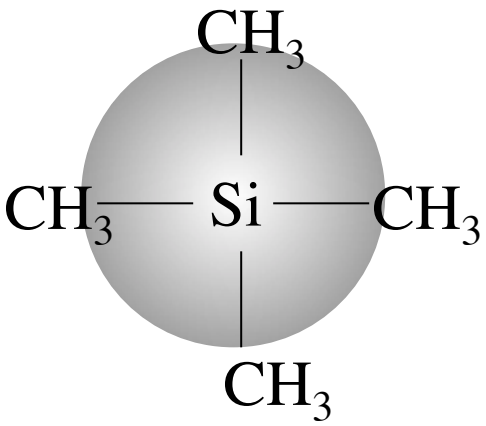
The electron cloud of the atom partially shields the nucleus from the surrounding magnetic field

When the carbon nucleus is adjacent to an electronegative atom, the carbon nuclei has fewer Electrons around it.



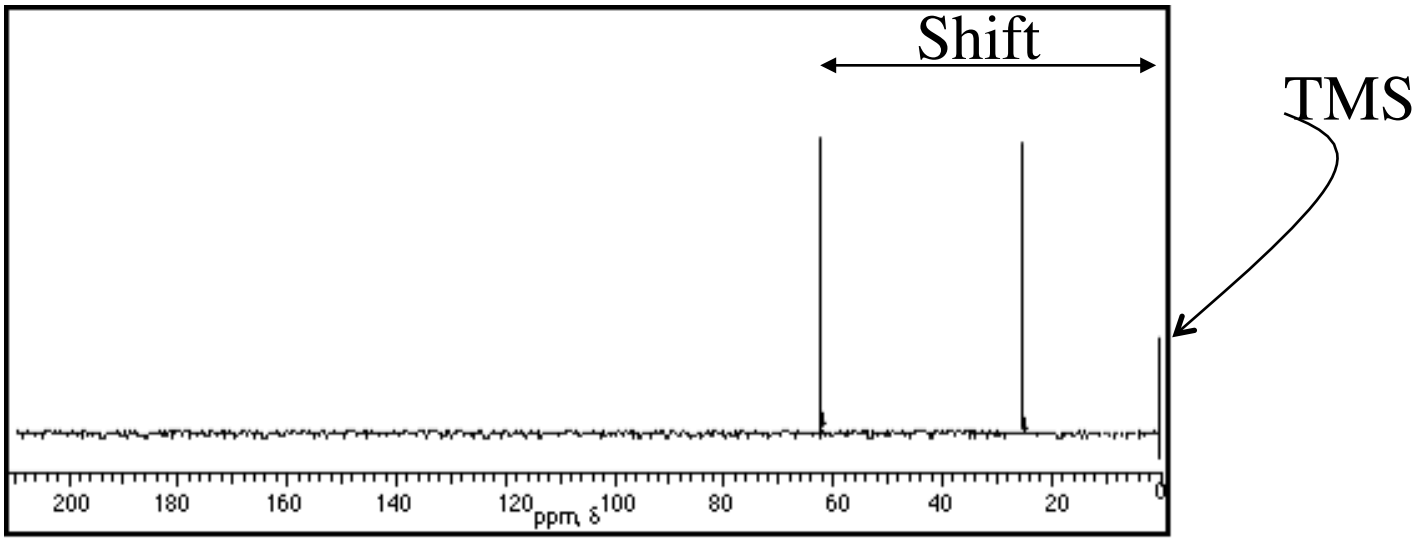
Nuclei with less electron density around them will resonate at a different frequency: It requires a weaker magnetic field to cause a carbon nuclei to resonate if it has less electron density around it.

Conversely atoms that donate electron density cause nuclei to resonate at lower frequencies (higher field strengths).



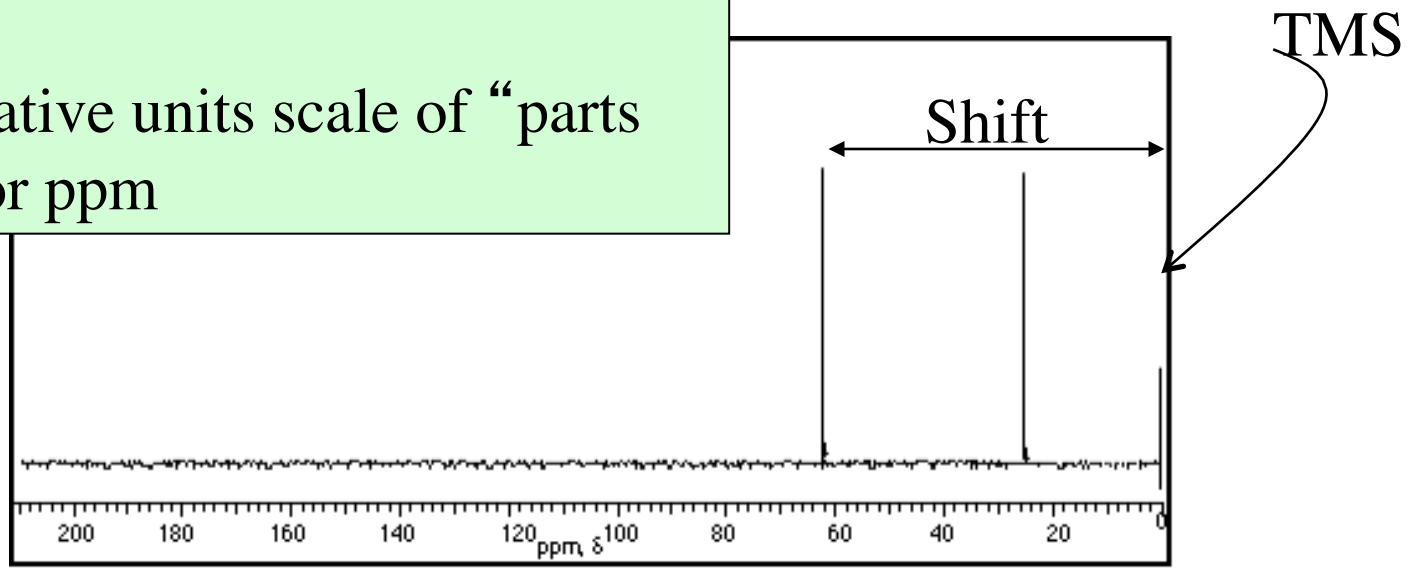
The silicon in tetramethylsilane (TMS) shields the carbon nuclei and makes them appear "up-field"

The chemical shift spectrum is measured relative to TMS.



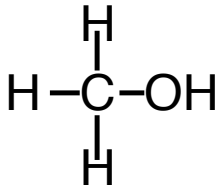
THE δ SCALE IS USED TO MEASURE CHEMICAL SHIFT

δ = is used to signify chemical shift.
Because the frequency depends on the field strength,
one uses a relative units scale of "parts per million" or ppm

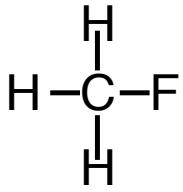


Chemical shifts reported as ppm units give the same values for the same compound regardless of the instrument used!

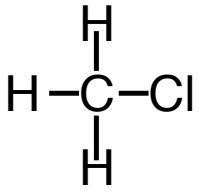
$$\delta = (\nu_{(\text{compound})} - \nu_{(\text{TMS})}) / \nu_{(\text{instrument field strength})}$$



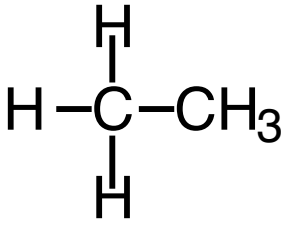
50.2 ppm



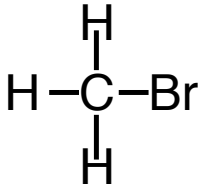
71.6 ppm



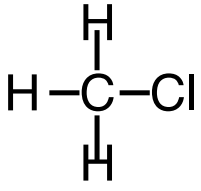
25.6 ppm



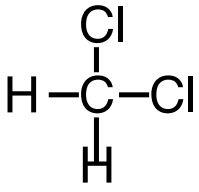
7.3 ppm



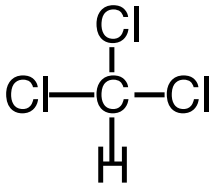
9.6 ppm



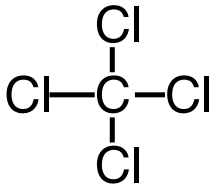
25.6



54.0

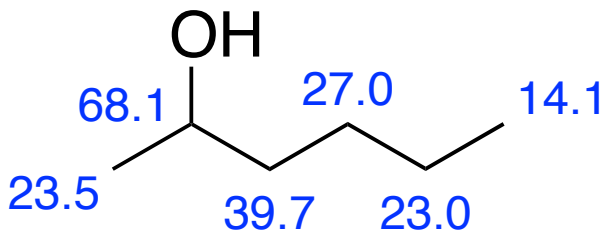


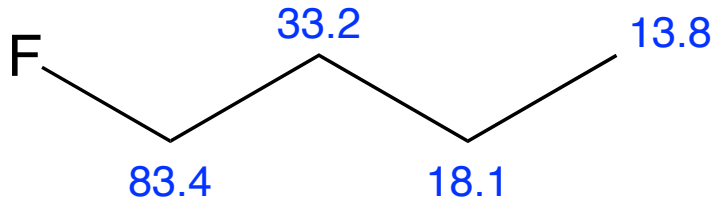
77.2



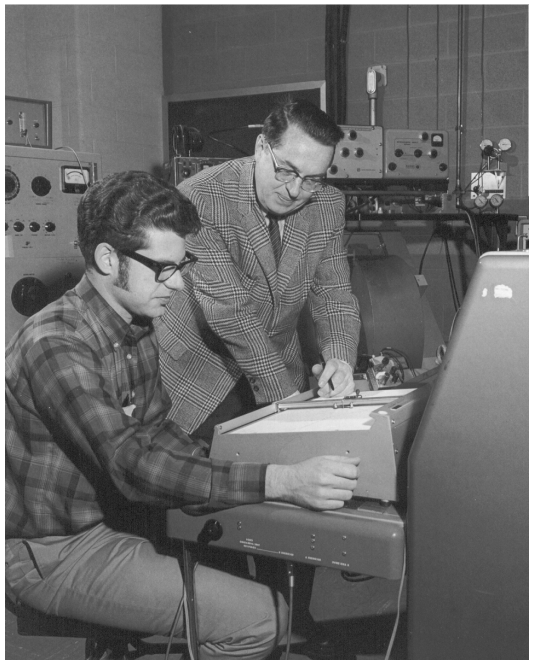
96.1

Atoms which are not directly attached to an electronegative atom are still shifted but the effect is significantly attenuated. The inductive effect (through bond influence) drops off rapidly with distance.



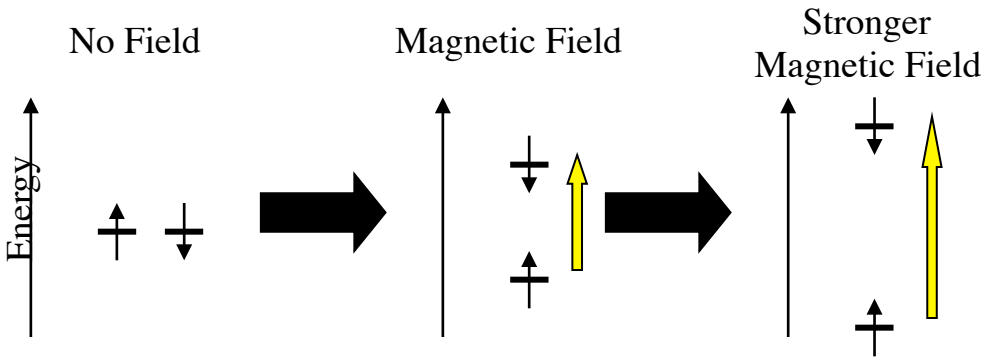


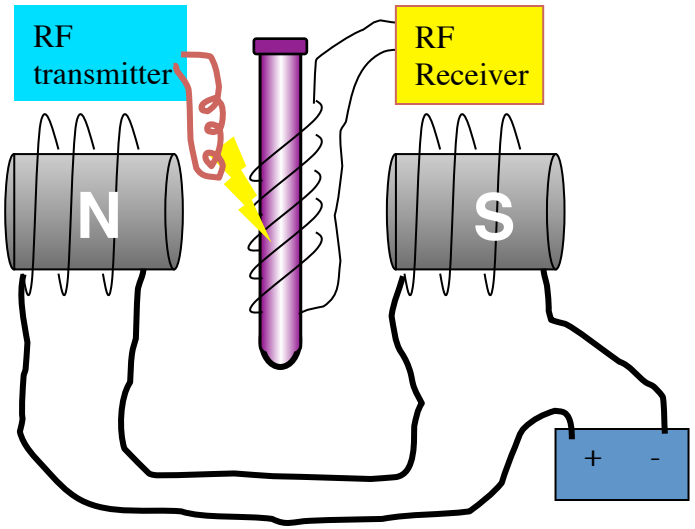
How do you take an NMR??

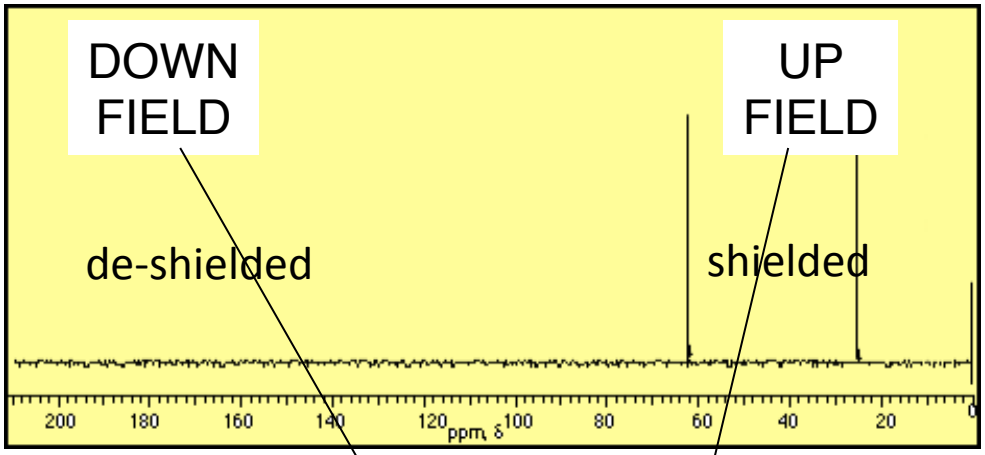


Max Tofield Rogers 1956

I. Constant Radio frequency but change magnetic field
OLD TRADITIONAL WAY!

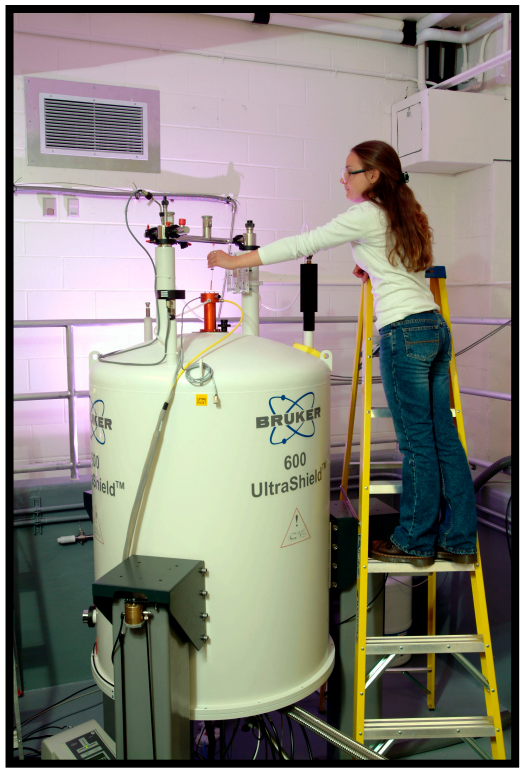


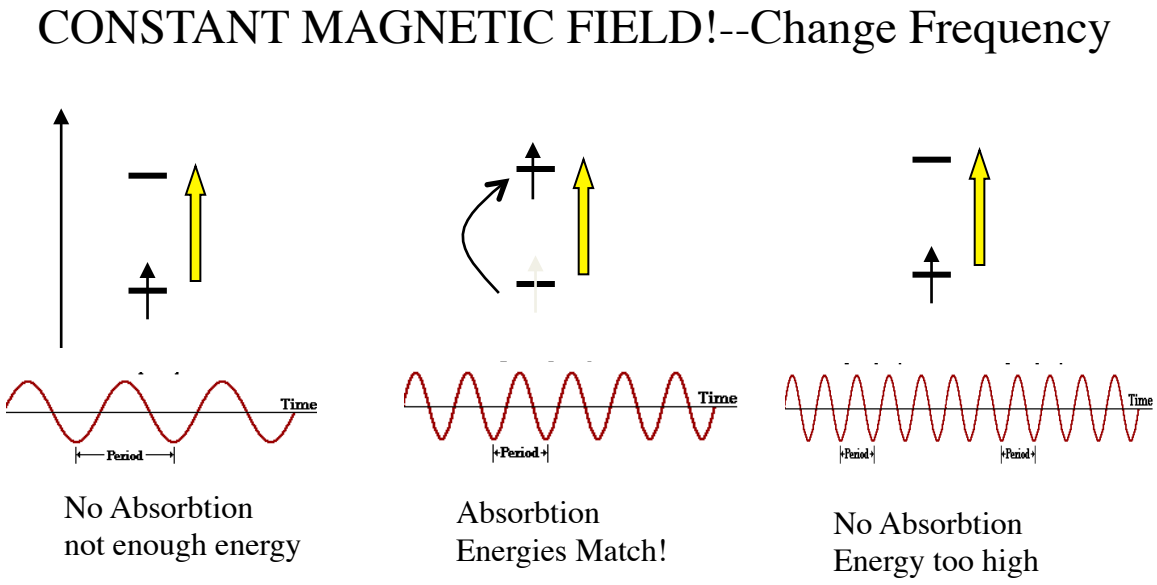




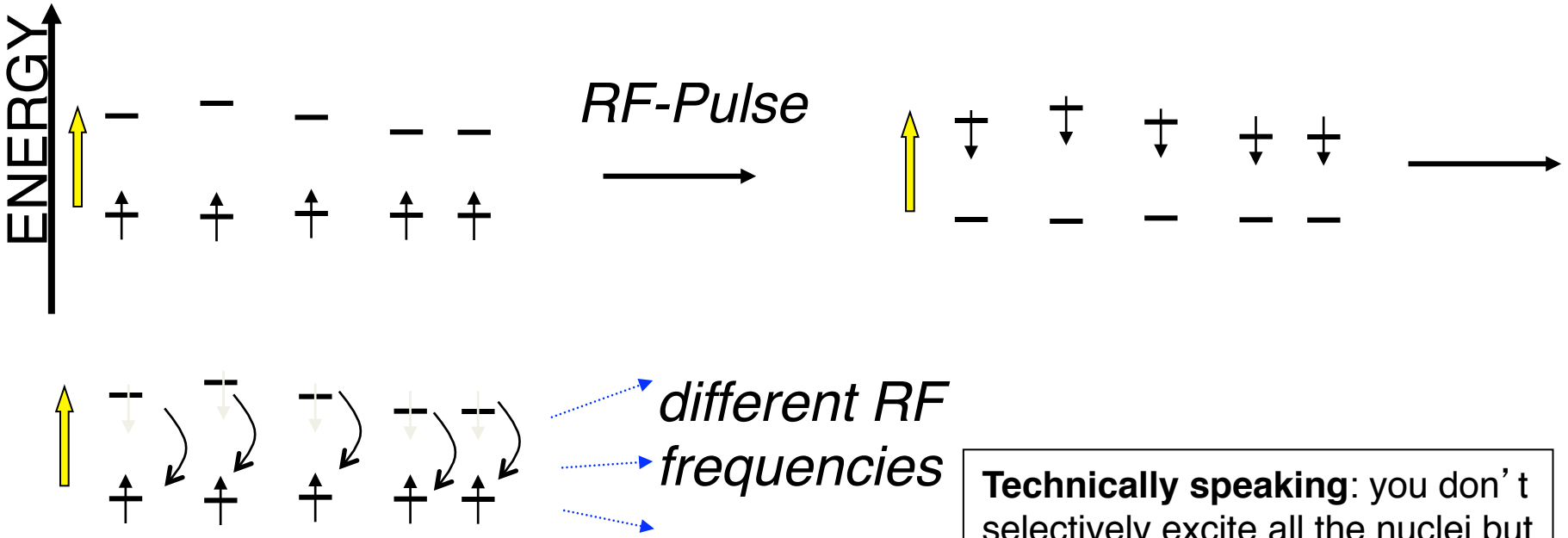
Know these terms!!

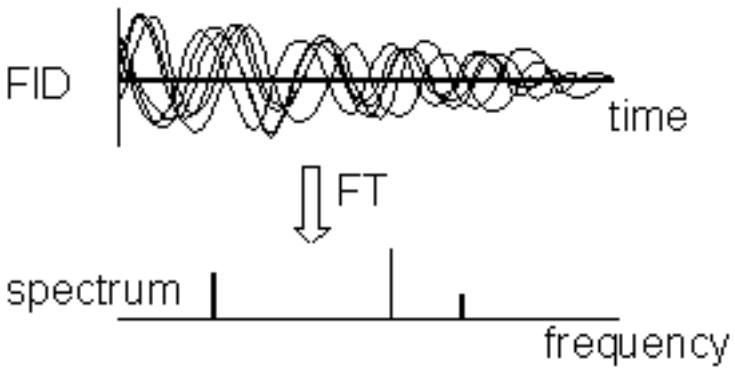
Technically Modern NMR spectra are obtained at constant field strength





FT-NMR

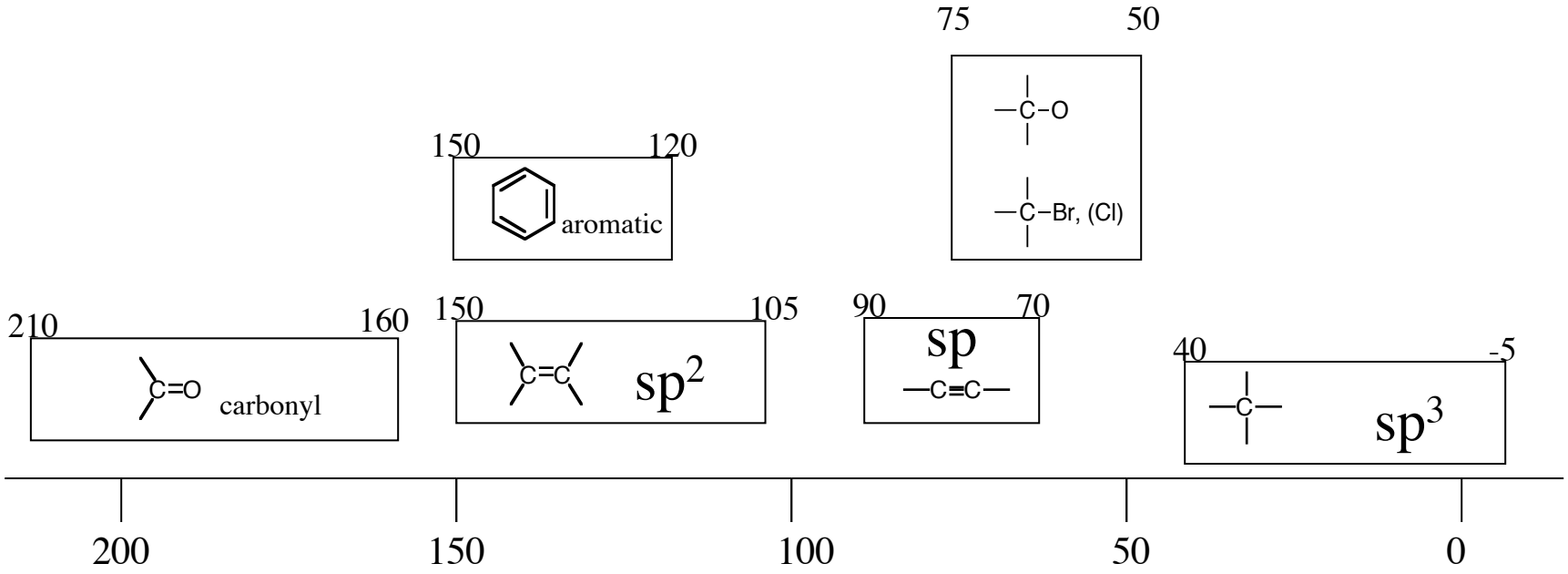




Technically speaking: you don't selectively excite all the nuclei but rather you saturate the exchange of nuclei between the upper an lower energy states. At equilibrium (in the absence of the RF energy) there are slightly more nuclei in the lower energy state than in the upper energy state based on the normal Boltzman distributions.

Typical Values of Chemical shift depend on the

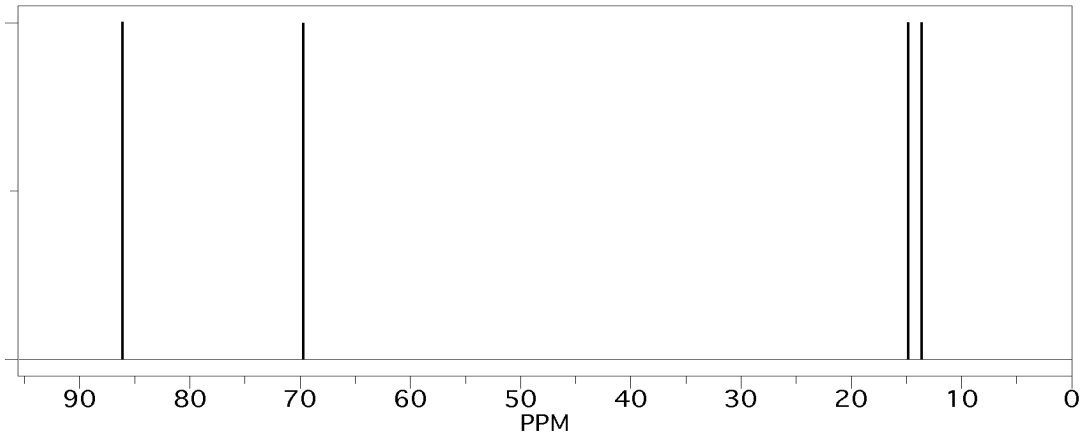
1. Hybridization
2. Electronegativity of attached atom(s).

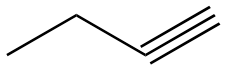


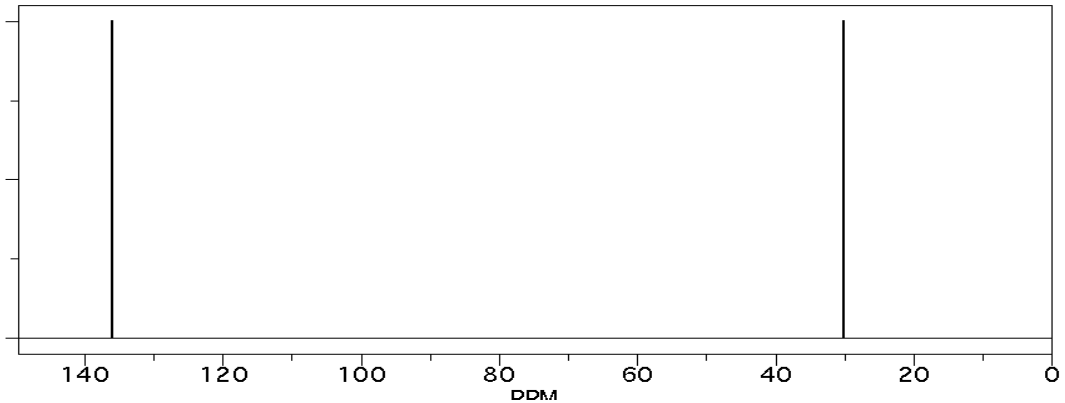
Some specific values are included in tables Section IV your text book!

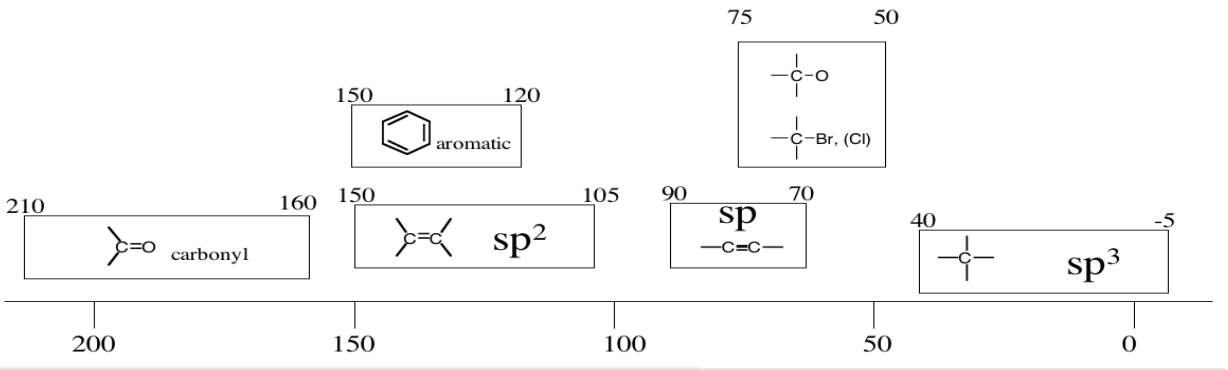
C_4H_6

IHD = 2

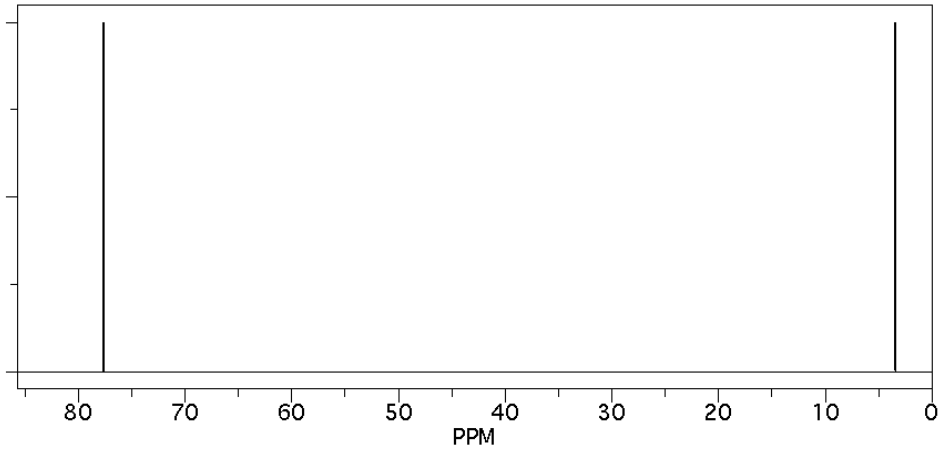

90
80
70
60
50
40
30
20
10
0
PPM

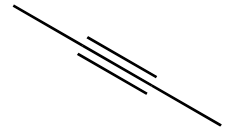


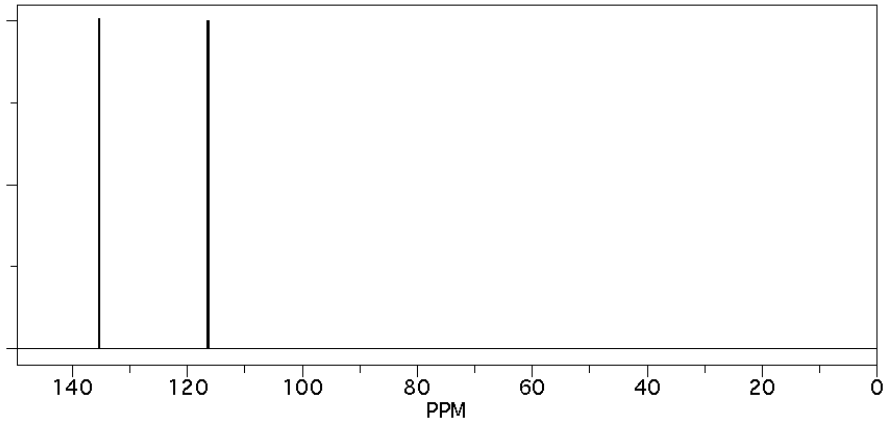

140
120
100
80
60
40
20
0

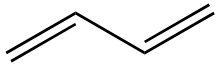

75
50
—C–O
—C–Br, (Cl)
150
120
aromatic
210
160
C=O
carbonyl
150
105
C=C
sp2
90
70
sp
—C≡C—
40
-5
—C—
sp3
200
150
100
50
0

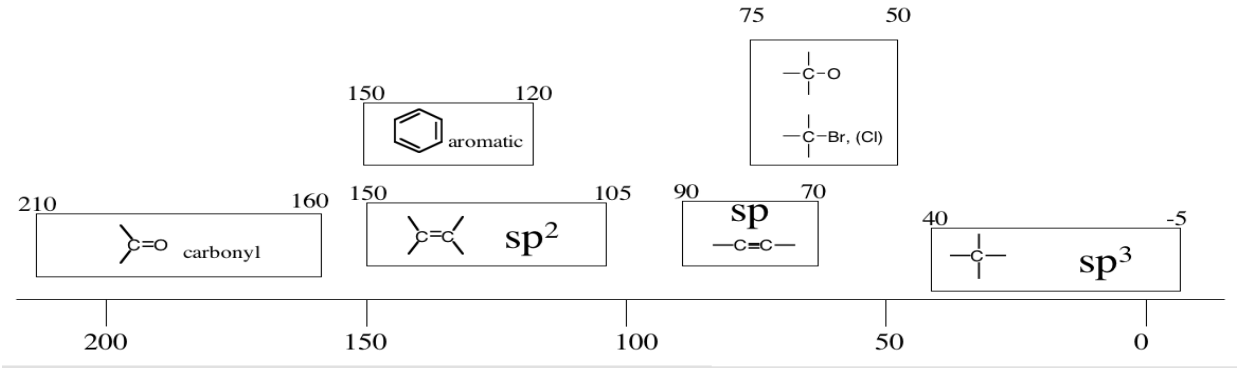
C_4H_6


80
70
60
50
40
30
20
10
0
PPM

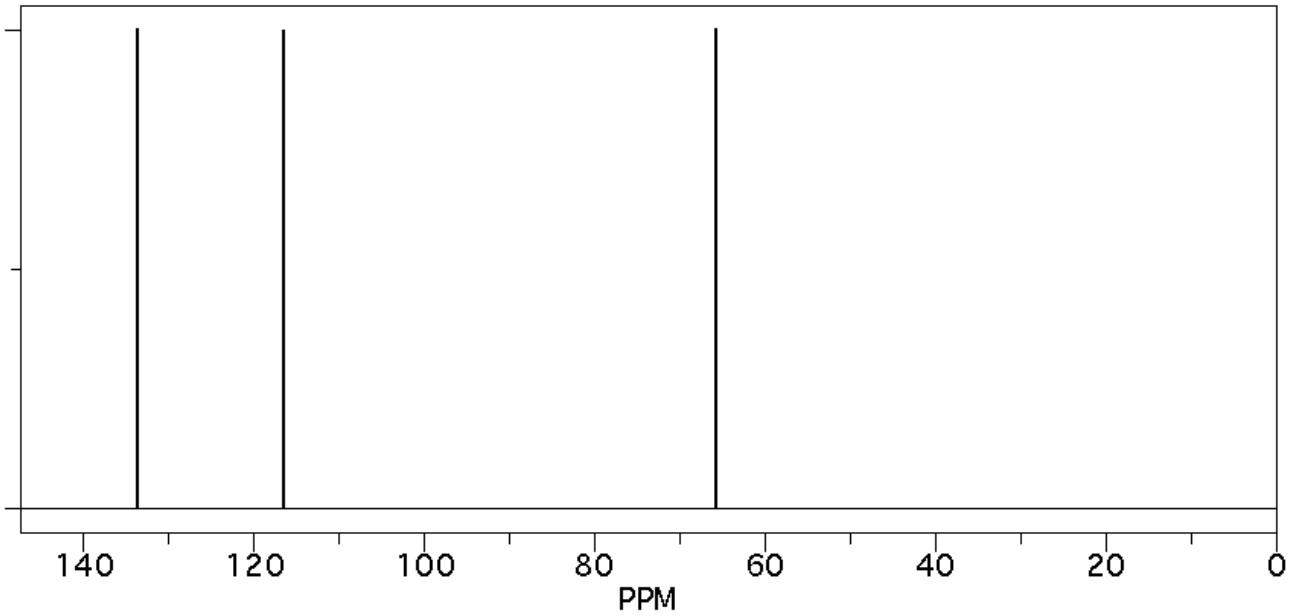


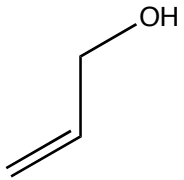

140
120
100
80
60
40
20
0
PPM



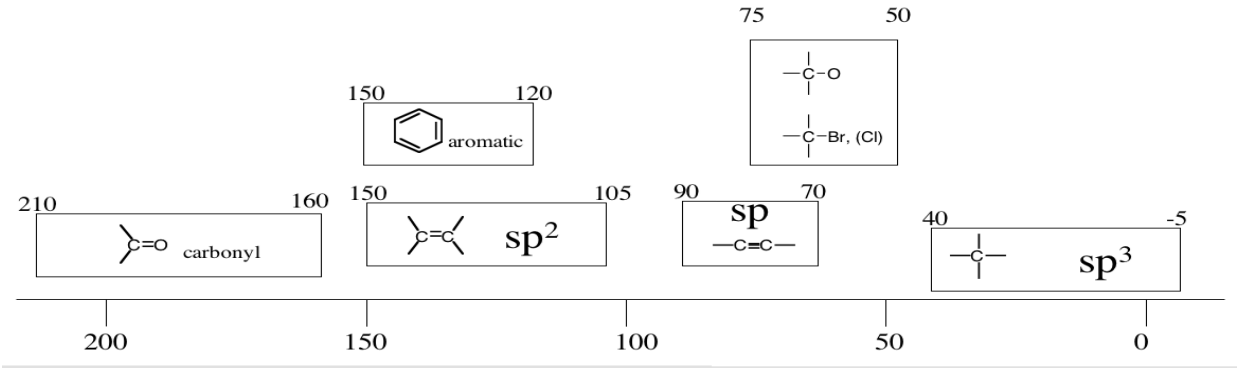

75
50
—C–O
—C–Br, (Cl)
150
120
aromatic
210
160
carbonyl
150
105
sp2
90
70
sp
—C≡C—
40
-5
sp3
200
150
100
50
0

C_3H_6O


140
120
100
80
60
40
20
0
PPM


OH

IHD = 1


75
50
—C–O
—C–Br, (Cl)
150
120
aromatic
210
160
carbonyl
150
105
sp2
90
70
sp
—C≡C—
40
-5
sp3
200
150
100
50
0